This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.
+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.
+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.
+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`

~~Sci 125.90~~ KF987

Bound

AUG 10 1909

Harvard College Library

FROM

The College

MEMOIRS

OF THE

COLLEGE OF SCIENCE AND ENGINEERING,

KYŌTO IMPERIAL UNIVERSITY.

VOL. I.

1903—1908.

KYŌTO.

1450-16

CONTENTS.

PAGE

Mitsuru Kuhara and Masumi Chikashige,—**Synthesis of Indigo and its Derivatives,** 1

Hanichi Muraoka and Takuro Tamaru,—**Ueber die Veranderung der elektrischen Leitungsfähigkeit eines Pulvers durch Induktion,** 20

Toshinojo Mizuno,—**On the Filings Coherer and Wireless Telegraphy,** 28

Toshinojo Mizuno,—**Electric Resonance,** 33

Eiji Aoyagi,—**A Graphical Representation of Potential Drops and Distribution of Currents in a Network System,** ... 40

Masumi Chikashige and Hitoshi Matsumoto,—**Defects of Uncarburetted Water-Gas as Fuel for Laboratory Use,** 55

Jisaburo Yokobori,—**On the Solubility of Gold-Silver Alloys in Potassium Cyanide Solutions,** 65

Tadasu Hiki,—**On the Allanite Crystal from Hiei Mountain,** ... 72

Sakuro Tanabe,—**Deflection and Vibration Diagrams of Kinokawa Railway Bridge Truss,** 75

Hitoshi Matsumoto,—**Note on the Body of Awata Pottery,** ... 77

Mitsuru Kuhara and Masumi Chikashige,—**Note on the Influence of Solvents upon the Formation of Chloracetyldiphenylamine,** 87

Yukichi Osaka,—**On the Distribution of Iodine between Two Solvents,** 93

Yukichi Osaka,—**On the Equilibrium of the Electrolytic Dissociation of Partially Neutralised Acids and Bases,** ... 103

Mitsuru Kuhara and Yoshinori Kishi,—**Action of Ammonia and of Amines upon Chloral,** 114

Tadasu Hiki,—**Occurrence of Cerasite and Chiastolite in a Metamorphosed Clay Slate,** 125

Sakuro Tanabe,—**Retardation Tests with an Unloaded, Covered Railway Wagon,** 137

PAGE

Kunito Ogawa,—**On the Electromagnetic Screening Effect of Metallic Conductors,** 140

Masumi Chikashige,—**Action of Alcohol upon Mercury Perchlorates,** 145

Yukichi Osaka,—**Reaction between Silver Nitrate and disodium Hydrogen Phosphate,** 158

Sadajiro Okada,—**Note on the Action of Phosphorus Pentachloride upon Tartranil,** 168

Yukichi Osaka and Jingoro Yamasaki,—**Equilibrium between Reciprocal Salt Pairs,** 173

Jingoro Yamasaki,—**Reaction between Carbonic Acid and Lead Acetate in an Aqueous Solution,** 176

Toshio Watanabe,—**Versuche zur Nutzbarmachung von Metallabfällen,** 183

Mitsuru Kuhara and Motooki Matsui,—**Formation of Amines from the Halogen Imido Esters,** 187

Daikichi Saito,—**Notes on the Refining of Copper,** 195

Yuko Mori,—**Electrolytic Dissociation of Partially Neutralised Weak Acids,** 205

Hanichi Muraoka,—**Ueber ein einfache Methode, den Grundton eines Klanges, dessen Höhe um ein Octave unsicher ist, zu entscheiden,** 211

Yoshisaburo Kashiwagi,—**Short Period Magnetographs,** 217

Taro Otake,—**On the Theory of the Rotary Converter,** 228

Mitsuru Kuhara and Tadaka Kainosho,—**On Beckmann's Rearrangement,** 254

Yukichi Osaka,—**Determination of the Solubility of a Given Substance by Means of Pulfrich's Refractometer,** 265

Jingoro Yamasaki,—**Reaction between Carbonic Acid and Lead Acetate in an Aqueous Solution. II.,** 275

Sakuro Tanabe and Kakutaro Hori,—**Dynamometer Car Experiments. Part I.,** 277

Motooki Matsui,—**Action of Hydrogen Sulphide upon Imidoesters,** 285

Yukichi Osaka,—**Determination of the Solubity of a Giv n Substance by Means of Pulfrich's Refractometer. II.,** ... 290

Yukichi Osaka,—**On the Birotation of d-Glucose. II.,** 304

PAGE

Kozo Ikawa,—**Kinetics of the Hydrolytic Decomposition of Methyl Acetate by the Catalytic Action of Acetic Acid,**... 320

Yogoro Kato,—**Physico-chemical Studies on Tofu,** 325

Yogoro Kato,—**The Electrical Conductivity and Dissociation of Sulphuric Acid in Aqueous Solutions at Higher Temperatures,** 332

Yogoro Kato,—**On the Reaction between Ferric Chloride and Potassium Ferricyanide,**... 352

Kozo Ikawa,—**Kinetics of Two Simultaneous Reactions in a System,**... 375

Motooki Matsui,—**Oxidation of Hydroquinone by the Catalysis of Carbon,** 386

Mitsuru Kuhara and Shigeru Komatsu,—**Isomeric Phenylphthalimides and some Allied Compounds,** 391

Tsutomu Shiomi,—**On the Solubility of Disodium Hydrogen Phosphate in Water,** 406

Masamichi Kimura,—**On the Dirichlet's Principle,** 414

Masamichi Kimura,—**Motion of a Negative Electric Charge in the Field due to an Electric Doublet,** 420

Shigeru Komatsu,—**Amine Salts of Phthalamic, Phenylphthalamic, and Phenylsuccinamic Acids,** 431

Sci 125.90
(Box on sh.)

MEMOIRS

OF THE

COLLEGE OF SCIENCE AND ENGINEERING,

KYŌTO-IMPERIAL UNIVERSITY.

VOL. 1., No. 1.

KYŌTO.

1903.

JUN 8 1901
CAMBRIDGE, MASS.

PUBLICATION COMMITTEE:

Professor	MITSURU KUHARA
Do.	HAN-ICHI MURAOKA
Do.	MASASHI NAMBA
Do.	SAKURŌ TANABE
Do.	TOSHINOJŌ MIZUNO.

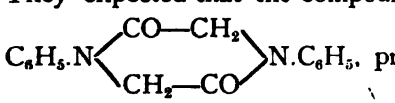
These Memoirs contain orgininal articles by the members of the University. They are not intended to be published at regular intervals. Each volume will be separated into 6 numbers of about 100 pages each.

Synthesis of Indigo and its Methyl Derivatives.[1]

By

M. Kuhara and **M. Chikashige.**

I. GENERAL CONSIDERATIONS.



In the course of the investigations on some complex compounds of the closed carbon-nitrogen nucleus, the authors saw an opportunity to try a new method for the formation of indigo. They expected that the compound called diphenyldiketopiperazine, $C_6H_5.N\left\langle\begin{matrix}CO—CH_2\\CH_2—CO\end{matrix}\right\rangle N.C_6H_5$, prepared by Abenius,[2] may split up on fusing with caustic potash into phenylglycocoll, which must instantly change by the further action of the alkali to pseudoindoxyl and finally the latter to indigo by oxidation, the last part of the reactions proceeding analogously to those of Heumann's synthesis.[3]

For the purpose of testing this view, diphenyldiketopiperazine was prepared from monochloracetanilide, $CH_2Cl.CO.NH.C_6H_5$, according to Abenius' directions, and the compound thus obtained was fused with caustic potash, by which process indigo blue was found to be formed, so that our assumption has been realized.

[1] The results of the work on this subject were already communicated to Am. chem. Journ. vol. XXIV, 167 and vol. XXVII, 1, and their summary is now given in this memoir.

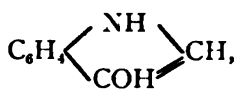
[2] Ber. d. chem. Ges., 21, 1665. The same compound was prepared by Hausdörfer by heating aniline, chloracetic acid and sodium acetate, and called by him diphenyl-α-γ-diacipiperazine.—Ber. d. chem. Ges., 22, 1797.

[3] Ber. d. chem. Ges., 23, 3043.

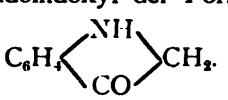
It will be remembered that some years ago Flimm[1] effected the synthesis of indigo by fusing monobromacetanilide,

$$CH_2Br.CO.NH.C_6H_5,$$

with caustic potash and subsequently oxidizing the aqueous solution of the product by air. The mechanism of the reactions in his process has, however, remained quite obscure to this time but has now, we believe, become clear by the authors' synthesis. He states: "Indigo wird nicht direct gebildet, sondern als erstes Condensationsprodukt des Monobromacetanilids entsteht Indoxyl,



oder vielleicht ein Pseudoindoxyl der Formel

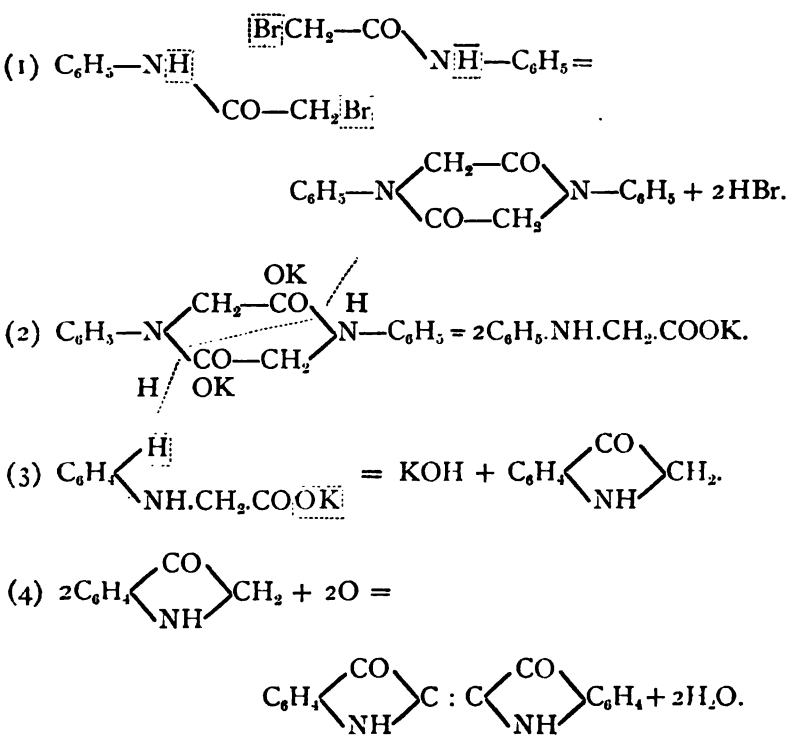


Dieses Zwischenglied geht durch Oxydation in Indigo über. Es ist mir nicht gelungen, dasselbe zu isoliren und rein darzustellen, da es äusserst unbeständig zu sein scheint. Besonders die Entstehung des Pseudoindoxyls hat die grösste Wahrscheinlichkeit für sich. Es tritt dann mit dem Brom ein Wasserstoffatom des Benzolkerns aus. Die Carbonylgruppe tritt an dessen Stelle, nämlich benachbart zum Stickstoff, und zwischen letzterem und der Methylengruppe findet einfache Bindung statt."

Heumann[2] also ventured to explain the nature of the reactions in Flimm's synthesis, and states: "Ehe aus jenem Körper (Monobromacetanilide) indess Pseudoindoxyl oder Indigo entstehen kann, musste zuerst eine Umlagerung zwischen den Gruppen CO und CH_2 erfolgen. Ob hierbei vielleicht als Zwischenprodukt das Bromid des Phenylglycocolls und, da Kali vorhanden ist, hieraus Phenylglycocoll resp. dessen Kaliumsalz entsteht, muss vorerst dahingestellt bleiben."

[1] Ber. d. chem. Ges., 23, 57.
[2] Ber. d. chem. Ges., 23, 3045.

The explanations by both Flimm and Heumann, with regard to the nature of the molecular rearrangement, which consists apparently of the mutual exchange of the positions of the groups CO and CH_2 are unsatisfactory. The authors have, however, found a more probable explanation in supposing that diphenyl-diketopiperazine may be formed from monobromacetanilide, as its first condensation-product, on fusing with caustic potash, the action of which is considered to be analogous to that of alcoholic potash, and that it may instantly split up into phenylglycocoll and the latter is in turn transformed to pseudoindoxyl and finally this to indigo. The series of the reactions involved in the formation of indigo from monobromacetanilide by the action of caustic potash may be represented thus:



If this view be correct, those substituted brom- or chlor-acetanilides which are so constituted as not to be able to form the piperazine ring would not yield indigo or its derivatives.

Now in order to decide the question, the authors have specially prepared methylchloracetanilide,

$$C_6H_5.N.CH_3.CO.CH_2Cl,$$

which is considered to be chloracetanilide in which the hydrogen of the imido group has been replaced by methyl, and hence can not form the piperazine ring. It was then subjected to fusion with caustic potash and found to decompose entirely, not giving a trace of indigo or its derivatives. Its deportment towards the fused potash was apparently different from that of ordinary chloracetanilide. Flimm[1] also states that phenylchloracetanilide,

$$C_6H_5.N.C_6H_5.CO.CH_2Cl,$$

prepared from diphenylamine and chloracetyl chloride did not give the phenyl derivatives of indigo at all under similar treatment. The authors repeated his experiments and obtained the same negative results, which must be due, as they believe, to the impossibility of the formation of the piperazine ring.

There is another fact which supports the authors' view. Hausdörfer[2] claims that he obtained phenylglycocoll by treating diphenyldiketopiperazine with alcoholic potash; we followed his method with diorthotolyldiketopiperazine and succeeded in getting a very small quantity of orthotolylglycocoll. Now we maintain that phenylglycocoll may be formed from diphenyldiketopiperazine by the action of fused caustic potash just as it is when alcoholic potash is used, and that indigo is formed by its further action.

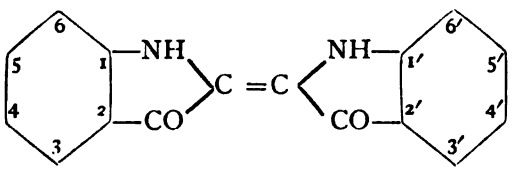
On extending such a principle of the synthesis of indigo to the formation of its derivatives, we succeeded in getting the different methyl derivatives. The experiments were conducted

[1] *Loc. cit.*

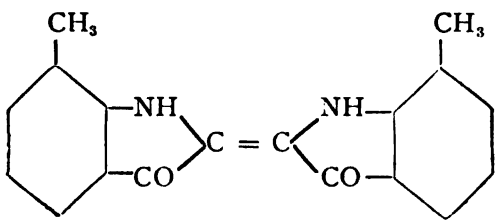
[2] Ber. d. chem. Ges., 22, 1802.

with chloracetyl derivatives of ortho-, meta- and paratoluidines as well as with diortho- and diparatolyldiketopiperazines, dimethylindigo having been obtained in each case. And also with chloracet-*unsym.*-metaxylide and chloracetpseudocumidide, and with their corresponding diaryldiketopiperazines, tetra- and hexamethylindigos were obtained.

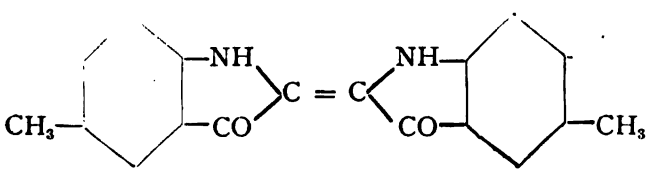
For designating the positions of methyl groups in the different methyl indigos, we propose to enumerate the carbon atoms in the two benzene nuclei of indigo, as shown in the following formula:



As only one dimethylindigo is possible from either diortho-tolyldiketopiperazine (or chloracetorthotoluide) or diparatolyldiketopiperazine (or chloracetparatoluide), we accept that the dimethylindigo from the former has the structure,



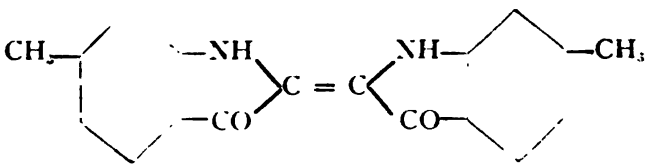
and we call it 6.6′-dimethylindigo, while from the latter we get



which is 4.4′-dimethylindigo.

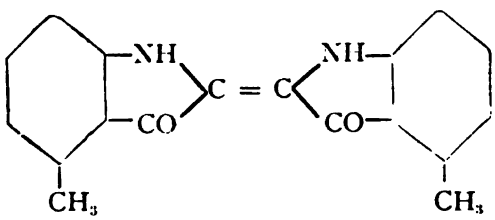
Three isomeric forms are possible from dimetatolyldiketopiperazine (or chloracetmetatoluide):

I.



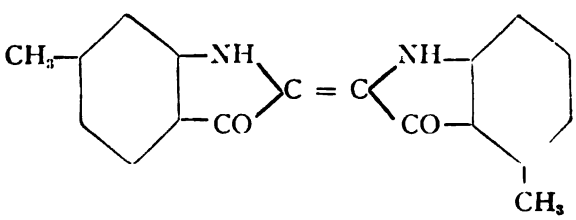
5.5′-Dimethylindigo.

II.



3.3′-Dimethylindigo.

III.

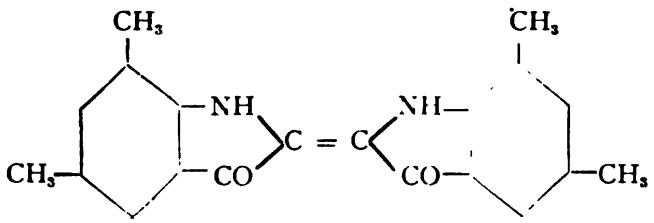


5.3′-Dimethylindigo.

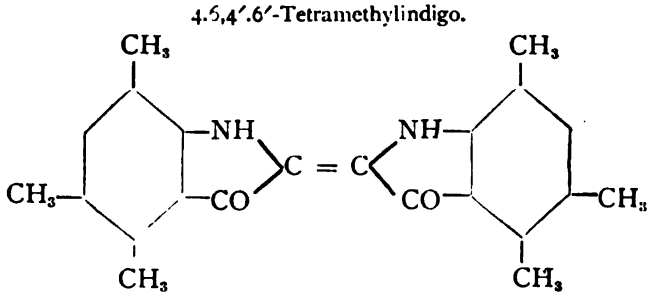
We must decide which of these three formulas corresponds to the dimethylindigo obtained by us from chloracetmetatoluide. Based upon the rules of orientation universally accepted, the CO group enters the para-position, with reference to the CH_3 group, more readily than the ortho-position, and hence the dimethyl-

indigo of the formula I, or 5.5′-dimethylindigo, may be the principal product of the reaction.

Tetra- and hexamethylindigo, formed respectively from di-*unsym*.-metaxylyldiketopiperazine or chloracet-*unsym*-metaxylide, and dipseudocumyldiketopiperazine, or chloracetpseudocumidide, must evidently possess the following structures:



4.6,4′.6′-Tetramethylindigo.



3.4.6,3′.4′.6′-Hexamethylindigo.

On referring to the literature, we find the different methyl derivatives of indigo which are already known. Dimethylindigo obtained by Flimm[1] from bromacetparatoluide, and that by Eckenroth[2] from chloracetparatoluide, the so-called *p*-dimethylindigo lately prepared by Kunckell[3] from *p*-methyl-*o*-acetylamidochloracetophenone, and 4,4′-dimethylindigo made by the authors from diparatolyldiketopiperazine are all identical. So-called metamethylindigo[4] was also prepared at Farbewerke, vorm. Meister,

[1] Ber. d. chem. Ges., 23, 59.
[2] *Ibid.*, 24, 593.
[3] *Ibid.*, 33, 2648.
[4] *Ibid.*, 16, 817 (Ber. ü. Pat.).

Lucius and Brüning from ortho-nitrometamethylbenzaldehyde, but its constitution is quite obscure, because, though it should be identical with either 4.4′- or 6.6′-dimethylindigo, interpreting its formation from the theoretical standpoint, it shows a spectrum entirely different from either of the other two, and consequently must possess a different structure. Flimm once tried to get an isomeric dimethylindigo from chloracetorthotoluide by the potash fusion, but having been unsuccessful, he ascribes the failure to the previous occupation of one of the ortho-positions by the methyl group. But the substance, like indigo, obtained from orthotolylglycocoll by the potash fusion at the Badische Anilin- und Soda-Fabrik[1] may be identical with our 6.6′-dimethylindigo prepared from diorthotolyldiketopiperazine or chloracetorthotoluide. And an indigo derivative obtained also at the Badische Anilin- und Soda-Fabrik[2] from metaxylylglycocoll and 4.6,4′.6′-tetramethylindigo obtained by us from di-*unsym.*-metaxylyldiketopiperazine or chloracet-*unsym.*-metaxylide, may possibly be identical.

Besides the formation of indigo or its methyl derivatives, as the principal reactions, from diphenyldiketopiperazine or other diaryldiketopiperazines, we have observed the production of the arylisonitrils, potassium carbonate, and primary and secondary amines, just as in the case of Heumann's synthesis. This decomposition also shows that the diaryldiketopiperazines may split up into the arylglycocolls which in turn would undergo the changes as in Heumann's process.

II. EXPERIMENTAL PART.

I. INDIGO.

Monochloracetanilide was prepared according to the directions given by P. J. Meyer[3] from monochloracetyl chloride. Following

[1] Ber. d. chem. Ges., 25, Ref. 488 (Ber. ü Pat.).
[2] *loc. cit,*
[3] Ber d. chem. Ges. 8, 1154.

for the most part the process described by Abenius for preparing diphenyldiketopiperazine from monochloracetanilide, the authors proceeded in the following way: A molecular quantity of monochloracetanilide was boiled for about five minutes with a molecular quantity of caustic potash dissolved in absolute alcohol. The potassium chloride precipitated was filtered and the alcohol removed from the filtrate by distillation. The residue which consisted mainly of diphenyldiketopiperazine was washed with hydrochloric acid to remove the aniline formed, and finally with ether. The substance was then purified by recrystallization from alcohol, and the crystals thus obtained were found to melt at 263° as Abenius had observed.

On subjecting a mixture of a certain quantity of diphenyldiketopiperazine and a little more than an equal quantity of dry powdered caustic potash in a glass vessel to fusion with sufficient care, the fused mass assumed finally a brownish-yellow color, while at the same time aniline and phenylisonitril were formed. The product, dissolved in water, instantly showed a blue color, and in a short time a blue powder settled at the bottom of the vessel. The blue coloring-matter, collected and dried, was tested. It was found to possess all the properties of indigo.

2. METHYLCHLORACETANILIDE,

$$C_6H_5—N\begin{cases} CH_3 \\ CO.CH_2Cl. \end{cases}$$

This substance has not been obtained to this time. At first methylaniline was prepared according to Hepp's[1] method. On mixing it with chloracetyl chloride, each in well-cooled ethereal solution, methylchloracetanilide was obtained in the form of a crystalline powder. It crystallizes from hot water in fine needles, but sometimes in large prisms from its dilute solution. It sublimes when heated and attacks the skin to some extent. The

[1] Ber. d. chem. Ges., 10. 327,

melting-point of the crystals is 61°. The crystals dried between the folds of filter-paper, or kept in a desiccator for a few days, gave on analysis the following results:

I. 0.4374 gram substance gave 0.0813 gram Cl.
II. 0.4998 gram substance gave 0.0919 gram Cl.

	Calculated for $(ClCH_2.CO.N.CH_3.C_6H_5)_2.H_2O$.	found. I.	II.
Cl	18.44	18.59	18.39

The crystals kept in a desiccator for more than a week were again analyzed.

0.1721 gram substance gave 0.0332 gram Cl.

	Calculated for $ClCH_2.CO.N.CH_3.C_6H_5$.	found.
Cl	19.35	19.29

Methylchloracetanilide, when fused with caustic potash, behaves quite idfferently from chloracetanilide or chloracettoluide. It never yields substances related to indigo but decomposes entirely.

3. DIMETHYLINDIGOS.

The chloracetorthotoluide used in the experiments was prepared according to the directions given by P. J. Meyer[1] whose process consists in mixing 1 molecule chloracetyl chloride with 2 molecules orthotoluidine, each in well cooled ethereal solution. Abenius and Widmann[2] recommends benzene as a solvent instead of ether. We have, however, found more advantageous, as we believe, to use the ethereal solutions of the two substances cooled with ice, so as to give the theoretical yield of the product.

Chloracetmetatoluide is not described in the literature. For its preparation exactly the same process as above given was used. The substance was purified by repeated recrystallization

[1] Ber. d. chem. Ges., 8, 1154.
[2] J. prakt. chem. [2], 38, 299.

from hot water and dried over calcium chloride, and its chlorine was determined.

I. 0.2510 gram substance gave 0.0481 gram Cl.
II. 0.2162 gram substance gave 0.0411 gram Cl.

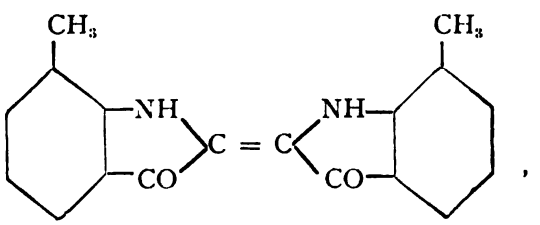
	Calculated for $CH_3.C_6H_4.NH.CO.CH_2Cl$.	Found. I.	Found. II.
Cl	19.35	19.17	19.05

It melts at 141°. It is somewhat volatile, even at ordinary temperature, and sublimes when heated. Its property of attacking the skin, its solubility and other properties are similar to those of the orthotoluide.

Chloracetparatoluide was prepared by Tommasi,[1] by Eckenroth and Donner[2] and by Meyer.[3] It was also prepared by the authors in the same way as the isomeric toluides.

From chloracetorthotoluide and chloracetparatoluide, diortho- and diparatolydiketopiperazines were prepared respectively by the process suggested by Abenius.[4] We were, however, not able to get dimetatolyldiketopiperazine, since only a few grams of chloracetmetatoluide were at hand. These diaryldiketopiperazines readily yield dimethylindigos.

1. 6.6′-*Dimethylindigo*,



was easily formed from diorthotolyldiketopiperazine as well as from chloracetorthotoluide by fusing with caustic potash.

[1] Bull. soc. chim., 19, 400.
[2] Ber. d. chem. Ges., 23, 3257.
[3] *Ibid.*, 8, 1154.
[4] *Ibid.*, 21, 1665.

Flimm states that he failed to get dimethylindigo from chloracetorthotoluide by fusing with caustic potash, but on the contrary we found that it could be formed from chloracetorthotoluide and also from its corresponding ditolyldiketopiperazine with a tolerably good yield. We mixed chloracetorthotoluide with an equal volume of dry powdered caustic potash, and heated the mixture in a test-tube or flask. The mixture instantly assumed a reddish-yellow color, when the potash began to fuse, then turned pale-yellow and reddish-brown, and finally changed to greenish-yellow on cooling. The mass was now treated with water, and from the solution dimethylindigo precipitated immediately on exposure to the air. Its production was shown to be dependent wholly upon the nature of the caustic potash used. When containing potassium carbonate, it was found to give the best result, and after several trials the following proportions of the materials were found to be most favorable:

Chloracetorthotoluide	100 parts
Dry powdered caustic potash	175 "
Potassium carbonate	25 "

Without mixing any potassium carbonate intentionally the yield of the dimethylindigo was very poor or often none. Its action is, however, not quite certain, but its presence may probably keep the mixture from being entirely fused when heated, thus avoiding the free access of air, and also preventing the violent action of the potash which would, in that case, be destructive. The use of a glass vessel should be avoided for fusion, since it is rapidly corroded by the melted potash. Thus a nickel crucible was substituted with the following precautions: A square box of asbestus-board, having a hole at its bottom just large enough to allow the crucible to rest over it, was constructed, and a cover of the same material was made to fit. A gas flame was applied from below, so as to heat directly the bottom of the crucible. We at first thought best to pass nitrogen gas into the box in order to prevent the oxidation of the product, but soon found unnecessary

to do so in consequence of the evolution of heavy vapors which fill the box and exclude air. The reactions proceeded smoothly.

For the purification of the dimethylindigo several methods were tried, and at last we found most advantageous to filter the precipitate of dimethylindigo and to wash successively with hot water and alcohol, the latter completely dissolving out the resinous matter. For analysis we had to sublime it under 35 to 40 mm. pressure, according to Sommaruga.[1] The sublimate was again washed with alcohol and ether to get rid of heavy hydrocarbons which have been formed by the decomposition of the dimethylindigo. The precipitated dimethylindigo can also be purified by washing with alcohol, then dissolving in hot chloroform and removing the insoluble impurities. This process is most convenient for purifying from silica which is derived from the glass vessels used.

The sublimed dimethylindigo was analyzed by Dumas' method.

I. 0.3158 gram substance gave 25.7 c.c. nitrogen at 14° and 756.7 mm. pressure.

II. 0.2158 gram substance gave 17.9 c.c. nitrogen at 20° and 756.4 mm. pressure.

	Calculated for $CH_3.C_6H_3\langle^{CO}_{NH}\rangle C:C\langle^{CO}_{NH}\rangle C_6H_3.CH_3$.	Found. I.	Found. II.
N	9.66	9.53	9.47

6.6′-Dimethylindigo is a powder when precipitated, but when sublimed it crystallizes in prisms very closely resembling ordinary indigo in appearance. It gives a bright violet vapor with partial decomposition when heated. Its characteristic property is its solubility in various solvents. One gram of the substance is soluble in about 2000 c.c. alcohol and in 500 c.c. chloroform. It is more or less soluble in ether, aniline, benzene, nitrobenzene, oil of turpentine, fused chloralhydrate, paraffin, linseed oil, acetic acid and fuming sulphuric acid, and in general more soluble than ordinary

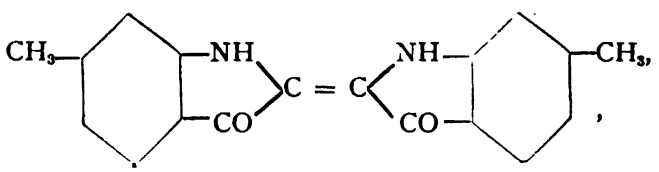
[1] Ber. d. chem. Ges., 11, 1355.

indigo. The colors of the solutions in these solvents vary from reddish-violet to green or blue. We observed the absorption band of the chloroform solution according to the statements of Krüss and Oeconomides,[1] seeking for the position of maximum darkness. When the solution is highly concentrated or its layer is thick, the absorption takes place from orange to green, while with ordinary indigo the range is much less. The results of the observations are given at the end of the paper.

In order to examine the products of the secondary reactions, we collected the fumes evolved during the fusion by passing them into a vessel containing water. Oily drops suspended in water were found to be orthotoluidine and methylorthotoluidine.

It will be unnecessary to describe the fusion of diorthotolyldiketopiperazine here, because its behavior toward caustic potash is precisely the same as that of chloracetorthotoluide. The dimethylindigo formed agrees in all respects with that from chloracetorthotoluide.

II. 5.5′-*Dimethylindigo*,



was formed from chloracetmetatoluide by the same method as its isomers, but the conditions of fusion were apparently different from the former cases. It seems strange that in this case the addition of potassium carbonate to the caustic potash was of no benefit; this may, probably, be due to the high melting-point of dimetatolyldiketopiperazine which is formed as an intermediate product in the reaction. Although we could not prepare it, as the quantity of chloracetmetatoluide at hand was very small, yet

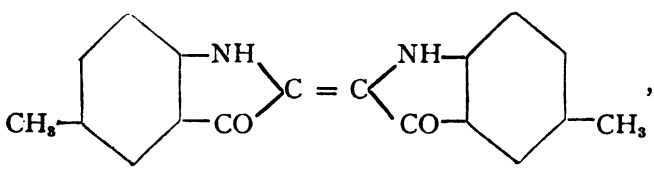
[1] Ber. d. chem. Ges., 16, 2051.

we infer that its melting-point may be higher than that of the ortho-compound, as will be seen from the following data:

	Melting-point.
Chloracetorthotoluide	111° to 112°
Chloracetmetatoluide	141°
Chloracetparatoluide	161°.5
Diorthotolyldiketopiperazine	159° to 160°
Dimetatolyldiketopiperazine	.....
Diparatolyldiketopiperazine	252° to 253°

5.5′-Dimethylindigo resembles its isomers in properties. It is soluble in alcohol, ether, chloroform, etc. Its solubility in chloroform is about 1 : 1000. It differs somewhat from its isomers in the absorption band, as will be seen in the annexed table.

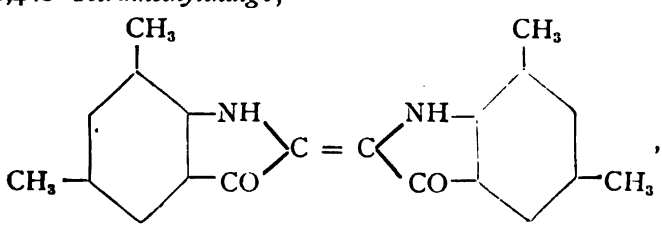
III. 4.4′-*Dimethylindigo*,



was formed from diparatolyldiketopiperazine and also from chloracetparatoluide under the same conditions as the meta-compound. It was found to be identical with the dimethylindigo already known, as explained in the preceding part of the paper. Its solubility in chloroform is almost the same as that of 5.5′-dimethylindigo.

4. TETRAMETHYLINDIGO.

4.6,4′.6′-*Tetramethylindigo*,



was formed from chloracet-*unsym.*-metaxylide and from di-*unsym.*-metaxylyldiketopiperazine by fusing with caustic potash. Its properties are similar, in many respects, to those of the other methyl derivatives of indigo. Its solubilities and the position of the absorption band are given in the table below.

Chloracet-*unsym.*-metaxylide was prepared by mixing 100 grams of *unsym*-metaxylidine and 50 grams of chloracetyl chloride, each dissolved in benzene. The yield was almost theoretical. It crystallizes in silky needles from benzene, and does not attack the skin. Its melting-point is 143°. The substance was analyzed with the following results:

I. 0.1141 gram substance gave 0.0204 gram Cl.
II. 0.1532 gram substance gave 0.0274 gram Cl.

	Catculated for $ClCH_2.CO.NH.C_6H_3(CH_3)_2$.	Found. I.	Found. II.
Cl	17.97	17.88	17.92

It produced di-*unsym.*-metaxylyldiketopiperazine by treating with alcoholic potash, as in the preparation of other diaryldiketopiperazines. It crystallizes in colorless needles and melts at 170°.

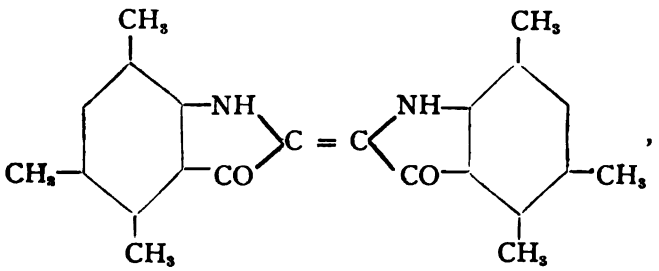
5. HEXAMETHYLINDIGO.

Chloracetpseudocumidide was prepared from pseudocumidine and chloracetyl chloride. It crystallizes in needles and melts at 158°.5. Its analytical results are as follows:

	Calculated for $ClCH_2.CO.NH.C_6H_3(CH_3)_3$.	Found.
Cl.	16.79	17.00

Dipseudocumyldiketopiperazine formed from the above substance crystallizes in colorless needles and melts at 221°.5.

The corresponding methyl derivative of indigo, or 3.4.6, 3′.4′.6′-hexamethylindigo,



was obtained from chloracetpseudocumidide as well as from dipseudocumyldiketopiperazine, but only in small quantity.

6. ABSORPTION BANDS AND SOLUBILITIES.

Positions of the Maximum Darkness in the Absorption Bands of Indigo and Methylindigos.
(*Chloroform Solutions.*)

	λ_1.	λ_2.	$\frac{\lambda_1+\lambda_2}{2}$
Indigo	622.7	587.6	605.1[1]
6.6′-Dimethylindigo	643.6	615.7	629.7
5.5′-Dimethylindigo	619.2	598.1	608.6
4.4′-Dimethylindigo	643.7	622.7	633.2
4.6,4′,6′-Tetramethyl-indigo	662.7	631.7	647.2

[1] Krüss and Oeconomides give $\frac{\lambda_1+\lambda_2}{2}=604.8$ for indigo.—Ber. d. chem. Ges., 16, 2051.

Solubilities of Indigo and Methylindigos in Various Solvents.

Solvents.	Indigo.	6.6′-Dimethylindigo.	5. ′-Dimethylindigo.	4.4′-Dimethylindigo.	4.6,4′.6′-Tetramethylindigo.
Alcohol.	Insoluble.	Soluble in cold; easily in hot with deep-blue color.	Soluble with blue color.	Soluble with blue color.	Soluble with blue color.
Ether.	Insoluble.	Soluble in cold with violet color.	Sol'ble with reddish-violet color.	Soluble with blue color.	Less soluble with blue color.
Chloroform.	Slightly soluble with violet color.	Easily soluble with violet color.	Readily soluble with reddish-blue color.	Readily soluble with blue color.	Easily soluble with deep-blue color.
Aniline.	Slightly soluble in hot with bluish-green color.	Soluble in cold with bluish-green color.	Soluble with greenish-blue color.	Soluble with blue color.	Soluble with green color.
Nitrobenzene.	Insol'ble in cold; soluble in hot with violet color.	Difficultly soluble in cold, readily in hot with violet color.	Soluble with green color.	Slightly soluble with green color.	Soluble with green color.
Turpentine oil.	Ins'l'ble in cold; slightly soluble in hot, but soon decolorizes.	Slightly soluble in cold, more so in hot, but soon decolorizes.	Soluble with blue color (slightly reddish) but soon decolorizes.	S'l'ble, but soon decolorizes.	Soluble with light blue color but soon decolorizes.

Solubilities of Indigo and Methylindigos in Various Solvents (Coutinued).

Solvents.	Indigo.	6.6-Dimethylindigo.	5.5′-Dimethylindigo.	4.4′-Dimethylindigo.	4.6,4′.6′-Tetramethylindigo.
Chloral hydrate (melt'd).	Soluble with deep-blue color.	Readily soluble with greenish-blue color.	Soluble with dark-blue color.	Readily soluble with bright-blue color.	Moderately soluble with greenish-blue color.
Paraffin (melt'd).	Slightly soluble with amethyst color.	Sol'ble with violet color.	Soluble with bright-violet color.	Soluble with blue color.	Sol'ble with violet color.
Linseed oil.	Sol'ble with violet color.	S'l'ble with reddish-violet color.	Soluble with reddish-blue color.	Soluble with green color.	Soluble with greenish-blue color.
Acetic acid.	Ins'l'ble in cold; slightly soluble in hot with blue color.	Difficultly soluble in cold, readily in hot with blue color.	Soluble with bright-blue col'r.	Soluble with blue color.	Soluble with blue color.
Benzene.	Slightly soluble in hot with amethyst color.	Soluble in cold, readily in hot with violet color.	Soluble with reddish-blue color.	Soluble with blue color.	Soluble with bluish-violet color.

Ueber die Veränderung der elektrischen Leitungsfähigkeit eines Pulvers durch Induction.

von

H. Muraoka und T. Tamaru.

Über die Leitungsfähigkeit eines Metallpulvers hat Hr. Sundorph[1]) den folgenden Versuch angestellt. In der Fig. 1 sind *A* und *B* zwei Metallstäbe, welche auf einer Glasplatte parallel in einer Entferung von mehreren Millimetern liegen. Die Stäbe sind mit den Polen eines elektrischen Elementes verbunden. Wenn man zwischen *A* und *B* Eisen- oder Nickelpulver zerstreut, so zeigt das Galvanometer *G* zunächst keine Ablenkung.

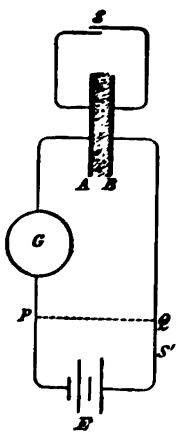


Fig. 1.

Sobald man aber mit dem Schlüssel *S* einen momentanen Schluss gemacht hat, so ist das Pulver ein guter Leiter geworden. Hr. Sundorph schreibt diese Erscheinung der durch den Kurzschluss entstandenen elektromotorischen Kraft zu, durch welche zwischen den Pulverteilchen Funken erzeugt werden, die das Pulver zusammenschmelzen.

Im Folgenden teilen wir einige Experimente mit, welche wir zum weiteren Studium dieser Erscheinung ausgeführt hahen. Da Hr. Sundorph nur mit Eisen und Nickel sich beschäftigt hat, so lag noch die Frage offen, ob diese Erscheinung von specifisch magnetischem Charakter sei. Wir wiederholten daher denselben Versuch mit Messingpulver und beobachteten die nämliche Erscheinung. Kohlenpulver zeigte schon vor dem Kurzschluss eine gewisse Leitung, sein Leitungsvermögen wurde durch den Kurzschluss bald kleiner und bald grösser. Frisch getrocknetes Kohlenpulver aber verhielt sich gerade entgegengesetzt, wie ein Metallpulver, indem sein Widerstand durch den Kurzschluss grösser wurde.

[1] Th. Sandorph, Wied. Ann. 68. p. 594. 1899.

Um zu sehen, ob die elektromotorische Kraft der Selbstinduction wirklich die Ursache der Erscheinung sei, machten wir den Kurzschluss an der Stelle PQ anstatt mit dem Schlüssel S (Fig. 1) und fanden, dass dann die Erscheinung ganz ausbleibt. Brachten wir zwischen P und Q einen Henrykasten und machten den Kurzschluss an der Stelle S', so wurde das Messingpulver dadurch gutleitend. Wurde aber der Henrykasten mit einer Capacität versehen, so blieb die Erscheinung wieder aus. Hierdurch ist es vielseitig bewiesen, dass die Selbstinduction des Galvanometers die Erscheinung bedingt. Ferner betrachteten wir das Messing- und Kohlenpulver durch ein Mikroskop und beobachteten deutliche Funken bei jedem Kurzschluss. Die Funken traten aber nur beim Oeffnen, niemals beim Schliessen auf. Ob dabei eine Schmelzung der Pulverteilchen eintritt, konnten wir nicht constatiren. Aber nach dem Umstande, dass beim Messing eine Begünstigung, bei der trockenen Kohle eine Zerstörung der Leitung durch den Kurzschluss verursacht wird, kann man vermuten, das bei jenem eine Schmelzung und bei dieser eine Zerstäubung der Pulverteilchen durch die Funken vor sich geht. Beim Messingpulver kommt es vor, dass durch das einmalige Oeffnen des Kurzschlusses wohl Funken überspringen, aber keine Leitung erfolgt. In diesem Falle treten bei dem nächsten Oeffnen wieder Funken auf. Ist aber die Leitung einmal zu stande gekommen, so giebt ein weiteres Oeffnen keine Funken mehr.

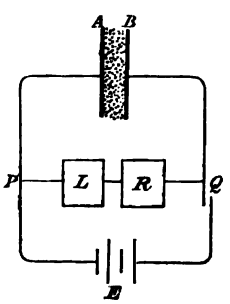


Fig. 2.

Um diese Erscheinung auch rechnerisch zu verfolgen, untersuchten wir, ob bei den Dimensionen unserer Versuche eine oscillatorische Entladung überhaupt möglich sei. Dazu berechnen wir nach Kirchhoff und Thomson das erste maximale Potential des Condensators. Wir betrachten nämlich die beiden Metallplättchen A und B der Fig. 2 (die Metallstäbe A und B der Fig. 1 wurden später durch parallele Plättchen ersetzt) samt dem Pulver als einen Condensator. Sei C

die Capacität in elektromagnetischem Maasse, R und L der Widerstand und der Coefficient der Selbstinduction des Schliessungskreises $APQB$, Q die Ladung, I die Stromstärke, V die Potentialdiffenrenz an dem Condensator, so gilt für einen Zeitpunkt t, nachdem der Kurzschluss geöffnet ist, die Gleichung:

$$RI = V - L\frac{dI}{dt}. \tag{1}$$

Da nun

$$\begin{cases} Q = VC, \\ I = -\dfrac{dQ}{dt} \end{cases} \tag{2}$$

ist, so wird aus (1):

$$-RC\frac{dV}{dt} = V + LC\frac{d^2V}{dt^2},$$

oder

$$LC\frac{d^2V}{dt^2} + RC\frac{dV}{dt} + V = 0. \tag{3}$$

Die Lösung ist

$$V = Ae^{\lambda t} + A'e^{\lambda' t}. \tag{4}$$

Aus (3) und (4) folgt:

$$LC\lambda^2 + RC\lambda + 1 = 0,$$

$$\lambda = -\frac{R}{2L} \pm \sqrt{\frac{R^2C - 4L}{2L^2C}}. \tag{5}$$

Sollte eine oscillatorische Entladung möglich sein, so muss in dem Ausdrucke (5)

$$R^2C < 4L$$

sein. Berechnen wir R^2C und L aus den Dimensionen unserer Versuchsvorrichtungen. Es waren bei einem Versuche unter anderen:

$$R \equiv 250 \text{ Ohm} \equiv 2{,}5 \;.\; 10^{11} \text{ E.-M.-E},$$
$$L \equiv 10 \text{ Milli-Henry} = 10^7 \text{ E.-M.-E.}$$

Die Capacität des Condensators berechneten wir vermutungsweise wie folgt: Bezeichnet l die Länge, b die Breite, d die Distanz der beiden Platten A und B (Fig. 2), so ist

$$C = \frac{l.d}{4\pi d} \cdot K \text{ in E.-S.-E.},$$

wo K die Dielektricitätsconstante bedeutet, wenn wir diese Benennung gebrauchen dürften. Dieselbe schätzten wir auf 100, aus folgender Ueberlegung.

Anstatt den ganzen Zwischenraum zwischen den Metallplättchen A und B mit Metallpulver zu füllen, denken wir uns 100 Metallscheibchen hineingelegt, sodass zwischen je zwei Scheibchen eine dünne Luftschicht entsteht, deren Dicke im Durchschnitte etwa $^1/_{100}$ jedes Teiles betragen mag. Jede Luftschicht hat dann eine Dicke von $^1/_{100} \cdot {}^1/_{100}$ von der ganzen Dicke d. Die Capacität des Condensators ist dann

$$C = \frac{l.b}{4\pi\left(100 \cdot \frac{d}{10\,000}\right)} = \frac{l.b}{4\pi d} \cdot 100,$$

sodass die Dielektricitätsconstante K etwa auf 100 zu schätzen kommt. Diesen Wert nehmen wir als annähernd richtig an.[1] Bei einem Versuche unter anderen waren nun:

$$l = 1{,}6 \text{ cm}, \quad b = 0{,}2 \text{ cm}, \quad d = 0{,}2 \text{ cm},$$

also

$$C = \frac{1{,}6 \cdot 0{,}2 \cdot 100}{4 \cdot 3{,}14 \cdot 0{,}2} = 13 \text{ E.-S.-E.} = 14 \cdot 10^{-21} \text{ E.-M.-E.}$$

Daraus bekommen wir

$$R^2 C - 4L = 875 - 4 \cdot 10^7.$$

Hiernach wird der Ausdruck unter dem Wurzelzeichen der Gleichung (5) negativ, und es muss eine oscillatorische Entladung stattfinden. Vernachlässigt man R^2C gegen $4L$, so wird aus (5):

[1] Sollte dieser Werth zehn oder hundert mal zu gross oder zu klein ausfallen, so hat das auf das folgende Resultat keinen Einfluss.

$$(6)\qquad \begin{cases} \lambda = -\dfrac{R}{2L} + \sqrt{-1}\sqrt{\dfrac{1}{LC}}, \\ \lambda = -\dfrac{R}{2L} - \sqrt{-1}\sqrt{\dfrac{1}{LC}}, \end{cases}$$

und aus (3)

$$(7)\qquad V = e^{-\frac{R}{2L}t}\left(A\cos\sqrt{\frac{1}{CL}}\,t + A'\sin\sqrt{\frac{1}{LC}}\,t\right).$$

A bestimmt sich aus der Bedingung, dass für $t = 0$, $V_{t=0} = V_0$ ist. Da die Schliessungswiderstände $\overline{AP}$ und $\overline{BQ}$ (Fig. 2) sehr klein sind gegen den Widerstand zwischen P und Q, so kann man schreiben:

$$V_0 = -I_0 R.$$

worin R den Widerstand zwischen P und Q bedeutet. Für A ergiebt sich also aus (7):

$$(8)\qquad A = -I_0 R;$$

Ferner bestimmt sich A' wie folgt. Es ist nach (2):

$$I = -\frac{dQ}{dt} = -C\frac{dV}{dt},$$

und aus (7) erhält man

$$\frac{dV}{dt} = -\frac{R}{2L}e^{-\frac{R}{2L}t}\cdot\left(A\cos\frac{t}{\sqrt{LC}} + A'\sin\frac{t}{\sqrt{LC}}\right)$$
$$+ e^{-\frac{R}{2L}t}\left(-A\sin\frac{t}{\sqrt{LC}} + A'\cos\frac{t}{\sqrt{LC}}\right)\cdot\frac{1}{\sqrt{LC}}.$$

Für $t = 0$ wird

$$\left(\frac{dV}{dt}\right)_0 = -\frac{R}{2L}A + \frac{A'}{\sqrt{LC}},$$

also

$$I_0 = -C\left(\frac{dV}{dt}\right)_0 - \frac{CR}{2L}A - \frac{CA'}{\sqrt{LC}},$$

woraus bei Vernachlässigung von $R^2 C$ gegen L folgt:

$$A' = -I_0 \sqrt{\frac{L}{C}}. \tag{9}$$

Führt man diese Werte von A und A' in (7) ein, so wird

$$V = -I_0 e^{-\frac{R}{2L}t}\left(\sqrt{\frac{L}{C}} \sin \frac{t}{\sqrt{LC}} + R \cos \frac{t}{\sqrt{LC}}\right). \tag{10}$$

Sucht man aus (10) die Bedingung für das Maximum von V, so erhält man

$$\operatorname{tg} \frac{t}{\sqrt{LC}} = \frac{2}{3} \sqrt{\frac{L}{R^2 C}} = \infty,$$

$$t = \frac{\pi}{2} \sqrt{LC}. \tag{11}$$

Führt man (11) in (10) ein, so erhält man, da

$$e^{-\frac{R}{2L} \cdot t} = 1$$

ist,

$$V_{\max.} = -I_0 \sqrt{\frac{L}{C}}. \tag{12}$$

Die maximale Dichtigkeit ist:

$$D_{\max.} = \frac{Q_{\max.}}{S} = \frac{C.\, V_{\max.}}{S.} = -I_0 \frac{\sqrt{LC}}{S}. \tag{13}$$

Da die Capacität

$$C = \frac{S}{2\pi d} \cdot K$$

ist, so folgt:

$$\left\{\begin{aligned} D_{\max.} &= -I_0 \frac{\sqrt{L}}{S} \sqrt{\frac{S}{4\pi d} K}, \\ &= -I_0 \sqrt{\frac{K}{4\pi}} \sqrt{\frac{L}{v}}, \end{aligned}\right. \tag{14}$$

wo v das Volumen des Pulvers bedeutet.

Die Gleichung (14) stellt die maximale Dichtigkeit des Condensators dar. Wenn man nun annimmt, dass die Widerstandsreduction des Metallpulvers bei einer bestimmten Dicke des Condensators, also bei einer gegebenen Anzahl von elektrisch effectiven Berührungspunkten der Pulverteilchen, mit der maximalen Dichtigkeit des Condensators zunimmt, so folgt aus (14) erstens, dass diese Widerstandsreduction, bei einer bestimmten Dicke des Condensators, mit inducirendem Strom zunimmt, und zweitens, dass dieselbe mit zunehmendem Volumen abnimmt.

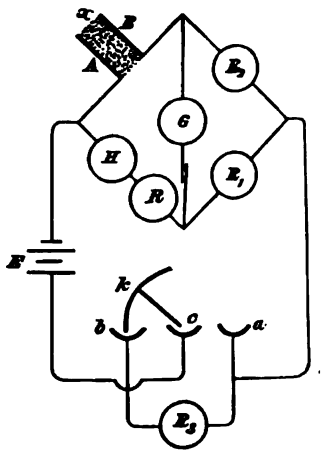


Fig. 3.

Um dies Resultat experimentell zu prüfen, haben wir eine Einrichtung getroffen, welche in der Fig. 3 angedeutet ist. *A B* ist der Condensator mit dem Metallpulver, *H* der Henrykasten, *k* ein Commutator, *a*, *b* und *c* sind Quecksilbernäpfchen, R, R_1, R_2 und R_3 Widerstandskasten. Zunächst wird *a* und *c* in Verbindung gesetzt; sobald diese unterbrochen und zugleich *b* und *c* in Verbindung gesetzt wird, geht der Strom durch den grossen Widerstand R_3, sodass die Ablesung des Galvanometers *G* möglich ist.

Der Widerstand x des Metallpulvers ist anfänglich sehr gross, nach der Induction reducirt er sich auf eine messbare Grösse. Wird das Pulver geklopft und wieder inducirt, so bekommt man wieder einen Widerstand von ungefähr gleicher Ordnung wie vorher. Wir haben daher das arithmetische Mittel aus mehreren Versuchen genommen. Folgende Tabelle enthält das Resultat aus einer Reihe von Massungen, bei welchen als *H* 10 Milli-Henry und als *E* 5 Daniell'sche Elemente gebraucht worden sind. In den letzten Columnen fehlen viele Zahlen, weil die Widerstandsreduction bei den schwachen inducirenden Strömen nicht mehr möglich war.

Inducirender Strom in Milliampère	$b = 2$ $d = 1$ $l = 1$	$b = 2$ $d = 4$ $l = 1$	$b = 2$ $d = 4$ $l = 2$	$b = 2$ $d = 4$ $l = 4$	$b = 2$ $d = 8$ $l = 2$	$b = 2$ $d = 16$ $l = 2$
	$v = 2$	$v = 8$	$v = 16$	$v = 32$	$v = 32$	$v = 64$ mm³
	Reducirter Widerstand des Messingpulvers in Ohm					
215	22,3	46,7	56	—	133	182
114	29,9	49	93	103	190	194
78	34,0	51	99	241	—	—
43,3	37,2	56	100	312	—	—
34,5	50,3	75	—	—	—	—
27,2	86,1	89	—	—	—	—

Diese Zahlen selbst, welche wir als Mittel aus je 20 Messungen zusammengesetzt haben, lassen eine quantitative Beziehung nicht finden. Qualitativ jedoch sieht man, dass die Widerstandsreduction um so kleiner ist, je kleiner der inducirende Strom und je grösser das Volumen ist, wie die Formel es fordert. Die im ersten Augenblicke paradox erscheinenden Zahlen der vierten und dritten Columne, dass der reducirte Widerstand bei dem grösseren Querschnitt $b.l = 2.2$ grösser ausfällt, als dei dem kleineren Querschnitt $b.l = 2.1$, finden nach der Formel (14) ihre Erklärung darin, dass bei der gleichen Dicke $d = 4$, also bei der gleichen elektaomotorischen Kraft, das Volumen bei jenem grösser ist, als bei diesem. Die Zahlen 100 und 190 bei gleichem Volumen in der fünften und sechsten Columne stehen mit den obigen nicht in Widerspruch, weil hier die Dicken d verschieden sind. Im allgemeinen aber ist das Phänomen von recht unregelmässiger Natur, sodass man ein verkehrtes Resultat erhalten kann, wenn man die Tabelle aus einer einzigen Versuchsreihe zusammenstellen wollte.

Endlich sei noch der folgende Punkt erwähnt. Es ist wohl jetzt die allgemeine Neigung der Pulvercohärer-Construction, das Volumen, welehes das Pulver einnimmt, möglichst klein zu nehmen. Diese Thatsache hat wohl ihren Grund darin, dass die Widerstandsreduction mit dem abnehmenden Volumen zunimmt und dadurch die Empfindlichkeit gesteigert wird, wie es nach dem obigen Resultate sein soll.

On the Filings Coherer and Wireless Telegraphy.

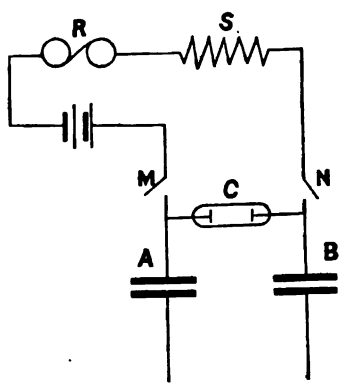
By

T. Mizuno.

As to the action of a filings coherer, several investigators have obtained different results and they maintain opinions more or less at variance with one another. Up to the present time, therefore, the question is not yet settled, and further research is still required.

I have recently made a study of the action of the coherer upon new lines. As shown in the annexed Fig. I, a filings coherer, *C*, was connected in series with two Léclenche cells, a relay, *R*, of a Morse's telegraphic apparatus, and a resistance *S*. To each of the terminals, *A* and *B*, of the coherer was attached a condenser of small capacity. Keeping the switches, *M* and *N*, out of the circuit, the condensers were put in communication with the poles of a secondary battery, whose voltage was 20 volts. By this process, the coherence of the filings was established, so that when I switched in *M* and *N* the bell of the Morse apparatus came into action: but this was not the case when the switches were closed beforehand and the process then repeated.

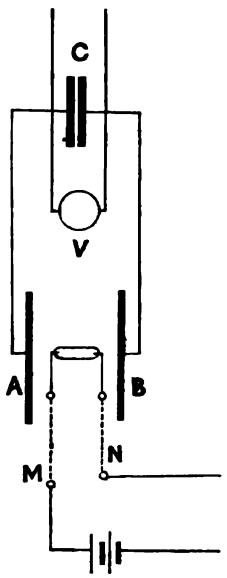
Fig. I.



I next tried another experiment in the manner indicated in Fig. II. *A* and *B* are two insulated brass plates, the dimensions

of each being 34 × 40 cm.s, and these were kept 16 cm.s apart. Each of the plates was connected with a Leyden jar, *C*, whose armatures were respectively joined to the poles of a Wimsharst's machine.

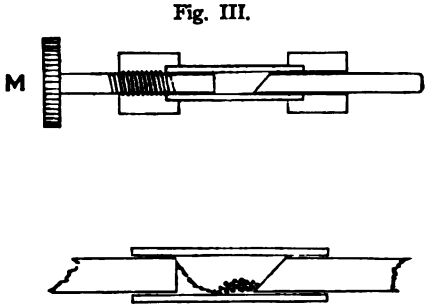
Fig. II.



The machine was slowly and uniformly rotated, so as to raise the potentials of the plates, *A* and *B*, to a given fixed value, the potential difference being read off by a Lord Kelvin's idiostatic voltmeter. Coherence took place in the coherer, placed between the plates, when the potential difference amounted to 500 volts. But this phenomenon did not take place when the switches, *M* and *N*, were first closed and the experiment then performed.

Thus, the two sets of the experiments just described point out that electro-static force is able to call forth mutual coherence of metallic filings. As affirmed by Lodge, the phenomenon of coherence necessitates the formation of metallic chains. Although it is indeed quite natural and reasonable to presuppose the formation of such chains, they have not, so far as I am aware, been actually observed. I made the attempt, however, and easily succeeded in actually forming the assumed chains. After the coherence of the filings was once established, I gently rotated the mill-head, *M*, of the electrodes belonging to the coherer, and the filings came out, one after another from the mass of filings, formeing a marked chain resembling in form a suspension bridge

Fig. III.



(See Fig. III). With care, this very interesting and noteworthy experiment can be performed any number of times. It is important to note that the number of cells used in this experiment was only two.

Is it not, then, rather surprising that such a small potential difference as two or three volts is sufficient to maintain the bond of a number of filings so as to sustain them in a suspended chain? The filings which compose the chain are, of course, separated from one another by a thin film of air, and such a film, when it is sufficiently attenuated, seems to conduct an electric current just as in the case of microphonic contacts. Therefore, the action of a coherer, subjected to the influence of an electro-static field, might be inferred from the above, and explained thus: in virtue of electric force, filings tend to arrange themselves in the direction of the force, so as to form the above-mentioned chain, invisible in this case, among themselves, and to acquire electric conductivity. Eccles[1] studied the degrees of coherence of metallic filings under the application of constant electromotive forces, and arrived at the conclusion that coherence is due to the self-arrangement of the filings in the direction of the acting electric force. Now, an oscillatory electromotive force is favorable to the formation of the chain just as much as is a constant one, and especially is it so when the amplitude of the oscillations is large. Here, in fact, lies the principle of my arrangement for wiercless telegraphy described below.

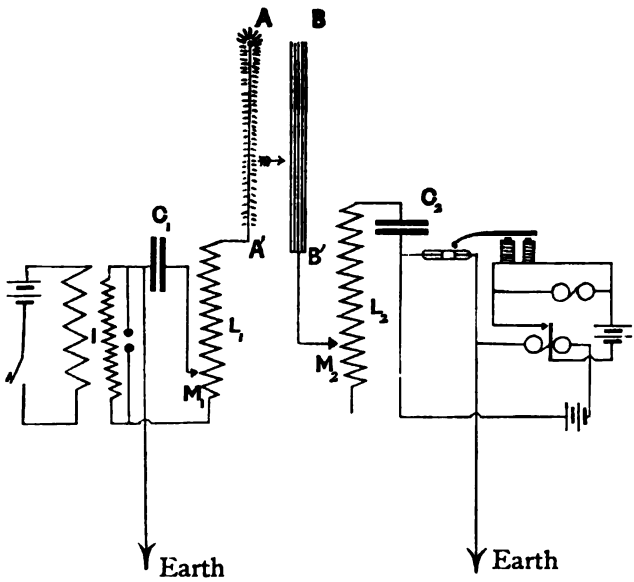
As the accompanying Fig. IV. shows, I use a primary oscillating circuit, consisting of a Leyden jar, C_1, and an inductive circuit formed by a portion of a coil L_1, To the free end of the latter coil is attached a vertical wire, AA', 12 metres in length, which serves as a sending air line.

Putting an induction coil, I, in action, a movable contact M_1 is adjusted till the coil is set in a state of violent resenance with the primary circuit. When this is attained, such powerful electric

The Electrician, Vol. 47, 1901, p. 682.

vibrations take place in the coil, that the wire, AA', when seen at night, sends forth vividly glowing brush discharges along its

Fig. IV.



whole length. The coil used in my experiment was an octagonal one, each of its sides being 26 cm.s wide, and its height 1,5 metres. It is the very same coil which I had formerly used in my researches on resonance coils.[1] The use of such a coil in wireless telegraphy is highly necessary because transmissable signal-distance depends solely upon the electric energy of the sender.

The receiver consists of a number of vertical, parallel wires, BB', all of them being joined up to a single wire at their lower ends. The latter wire leads through a window to a coil, L_2, with an adjustable contact, M_2. Instead of connecting the end of the coil directly with the coherer, as is commonly done in some of the prevailing systems, it is joined to one of the armatures

The Electrician, vol. 51, No. 16, Aug. 1903.

of a mica-plate condenser, C_2, of very small capacity. The coil and the coherer being thus interrupted by the condenser, the oscillatory electrical impulses given to one of the electrodes of the coherer are much more intense than with some of the prevailing systems. For, in the above arrangement, when the coil, L_2, is brought into resonance with the primary coil, L_1, the plates of the mica-condenser, and consequently the electrode of the coherer form the potential loop of electric vibrations. My arrangement, as described, was tried with the expected success in the garden of our physical laboratory, and I hope to increase my working distance and to carry out the experiment on a larger scale.

Electric Resonance.

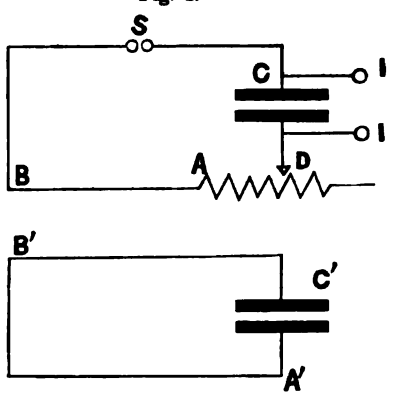
By

T. Mizuno.

Since electric resonance is of much interest and great imprtance, it is highly desirable to contrive some means for representing resonance phenomena qualitatively. The following arrangements, I think, well answer to this requirement.

A primary oscillator consists of a single turn *ABS* of copper wire, with an adjustable self-induction *AD*, conneted at its one end, through a spark gap *S*, with one of the armatures of a Leyden jar *C*. (Fig. I.) In front of, and at a certain distance from, the turn *ABS*, there is placed a resonator consisting of a few turns of copper wire whose extremities are respectively connected with the armatures of a Leyden jar *C'*. Both the oscillator and the resonator circuits are fastened to a vertical rectangular wooden frame whose sides are 68 and 90 cm.s respectively.

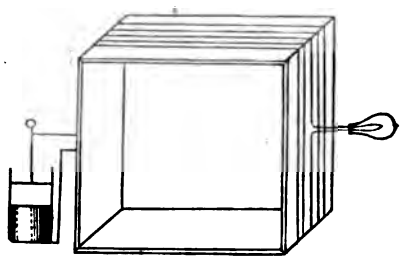
Fig. I.



In the resonator, somewhere near its middle part, an incandescent lamp is inserted as shown in Fig. II. Putting the induction coil I in Fig. I. into action, and properly adjusting the self-induction in the oscillator by means of a movable contact-piece *D*, the mutual resonance of the oscillator and the resonator can be established. In consequence of the resonance, an oscillatory current, with an intensity otherwise unattainable, flows in the resonator, and the lamp is lighted.

Now, either increasing or diminishing the self-induction of the oscillator from the value just corresponding to the resonance, the glow of the lamp decreases in its intensity and finally fades away. In my experiments, I used 50, 5, and 2-volt lamps as the case required.

Fig. II.



It is important to note that in the neighborhood of the oscillator, the resonance phenomenon is masked, to a large extent, by the effect due to the forced oscillations. Thus, at the distance of about 10 cm.s from the oscillator, it was found that a 50-volt lamp lighted well, even when there was no syntonization in the resonator. Hence, under such a condition, we are not able to bring out a well-marked resonance phenomenon. As a distance from the oscillator increases, however, the effect of the forced oscillations becomes weak, and the resonance effect comes into predominance. In this case, it is of course necessary to employ a lamp of less voltage, simply because the amplitude of the impressed oscillations is proportionally decreased. At a distance of about 50 cm.s, I used a 5-volt lamp, and a very sharp resonance was observed.

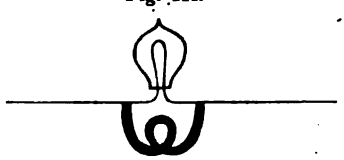
Again, placing the resonator at a distance nearly equal to 30 cm.s, and doubling the capacity of its jar (0,0035 microfarad in my experiment), I was enabled to observe the resonance due to the first harmonic, i.e. the octave of the vibrations in the oscillator. In other words, having first syntonized the oscillator, whose capacity is 0,0034 microfarad, to the resonator so as to set the 2-volt lamp in incandescence, the self-induction of the oscillator, was diminished, and at a certain stage the incandescence re-occured. Doubling the capacity of the resonator was found to be necessary, as a much wider range of variations must be given to the adjustable self-induction of the oscillator in order to bring out the octave.

So far as the visible effect alone is concerned, the most sensitive detector of the resonance phenomena is an adjustable point-sphere spark micrometer. Replacing the lamp in Fig. II. by this micrometer, we get a new resonator, and with this resonator I was enabled to observe the resonance spark up to a distance above two metres from the oscillator. The point of the micrometer consisted of an ordinary sewing-needle. In the neighborhood of the oscillator, between the point and the sphere of the micrometer, there occur brush-like sparks, intense enough to be visible at a great distance.

It is here disirable to remark that by increasing the electrical dimensions of both oscillator and resonator the resonance effects can be much augmented and consequently they can be observed at a still greater distance.

Next, a well-known impedance effect of rapidly oscillating currents can be easily shown by means of the above arrangement. To do this, we have only to shunt the lamp in Fig. II. by a single or by double turns of a thick copper wire, as indicated in Fig. III. The resonance current then passes freely through the lamp, as if there were no additional inductive loop, and consequently the luminosity of the lamp is not affected to any appreciable extent.

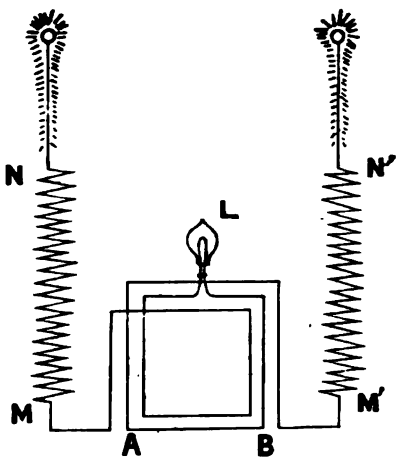
Fig. III.



Again, we can also beautifully show a resonance phenomenon occuring in an open circuit. Taking away the condenser from the rectangular resonator in Fig. I, two vertical wooden cylindrical coils *MN* and *M'N'* of the same dimensions (each of the coils used by me was 76 cm.s in height, 9,2 cm.s in diameter, and wound with bare copper wire 1 m.m in diameter, the total number of turns being 180) are respectively connected with the ends of the resonator as shown in Fig. IV. A 5-volt lamp L is inserted at the middle part of the rectanguler portion of the circuit.

Thus the rectangular circuit, AB, together with the coils attached at its ends, forms an open circuit. The system is now placed in front of the oscillator at a distance of a few centimetres from the latter. Properly adjusting the self-induction in the oscillator, we can throw the system into violent resonance. The straight wires attached to the free ends of the coils *MN* and *M′ N′* then emit powerful brush discharges, and at the same time the lamp *L* is brought into incandescence.

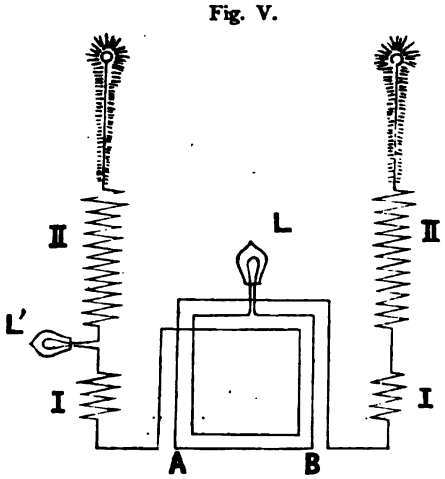
Fig. IV.



The capacity of the Leyden jar of the oscillator used in the experiment = 0,00075 microfarad.

It is not of course necessary to confine the lamp to the middle part of the circuit. Provided the distance from the latter part be not too far, we may place a lamp there, and the latter can be also set in incandescence. Thus two coils I and II, having lengths in the ratio about equal to 1 : 2, are joined in series and conneted with each end of the rectangular circuit, *AB*; and in addition to a 2-volt lamp *L* placed at the middle part of the circuit, another lamp *L′* of the same voltage is inserted between the coils I and II. (Fig. V.) We can

Fig. V.



then manage the experiment so as to simultaneously put the two amps into incandescence. In this case, the lamp L emits light most intensely, while L' moderately, the gradations of the intensities of the oscillating current along the circuit being thus well depicted.

Next, properly reducing the self-induction in the oscillator, we can also call forth a second resonance in the open circuit. This corresponds to the first odd harmonic of the electric vibrations in the oscillator, and it is very interesting to observe that, while the lamp L lights up well and the terminal wires give out vivid brush dircharges as before, the incandescence of the lamp L' totally ceases and a mere electro-statical glow takes place therein.

In fact, the electric vibrations in the resonantor just described correspond to elastic vibrations of a rod fixed at its middle part. As can be mathematically shown, in the case of the fundamental vibrations the potential is a maximum at the free ends of the coils and a minimum at the middle part of the rectangular portion AB, whilst the oscillating current possesses its loop at the latter part and its nodes at the free ends. In the case of the first odd harmonic vibrations, the free ends of the open circuit and the portion L' constitute the parts of the maximum potential vibrations, and since the phases of the potential and current vibrations differ by a quarter-period from one another, a mere electro-statical glow of the lamp L' in this case is self-evident.

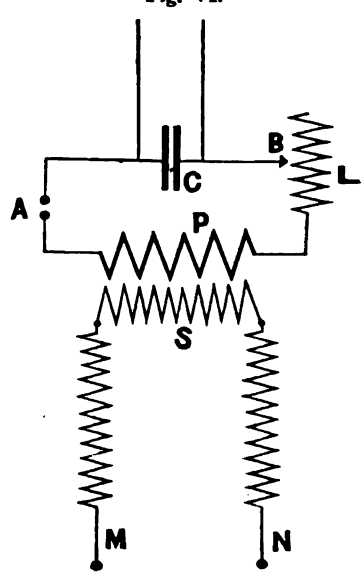
The incandescence of the lamp in the two cases is especially interesting, because in the cases under consideration the circuit is quite open, while in the case of the resonator containing a condenser, the circuit is, in reality, closed by the so-called Maxwellian displacement current in the dielectric of the condenser.

Now, the above modes of experimenting are very advantageous, because we can observe simultaneously the characters of both the potential and current vibrations in an open circuit. This advantage of the arrangement arises from the fact that we use coils of great self-induction. For the brilliancy of a resonance phenomenon

is solely determined by the amount of the electric energy expended, and the greater the self-induction of the resonantor, the larger capacity we can take in the oscillator. Sets of all the experiments described above can be performed without difficulty when the principle is once grasped, and they furnish us very convenient means for lecture demonstrations on electric resonance.

Befor concluding, I shall here describe a simple convenient resonance apparatus. A well-known Tesla coil is a resonance one, and by means of it the phenomena peculiar to the electric currents having high frequencies may be studied. But Tesla's apparatus posesses some disadvantages. For, firstly, the apparatus requires a somewhat awkward oil insulation, and secondly the primary and secondary coils are each fixed in its electrical dimensions. A new apparatus devised by me, however, is quite free from such inconveniences.

Fig. VI.

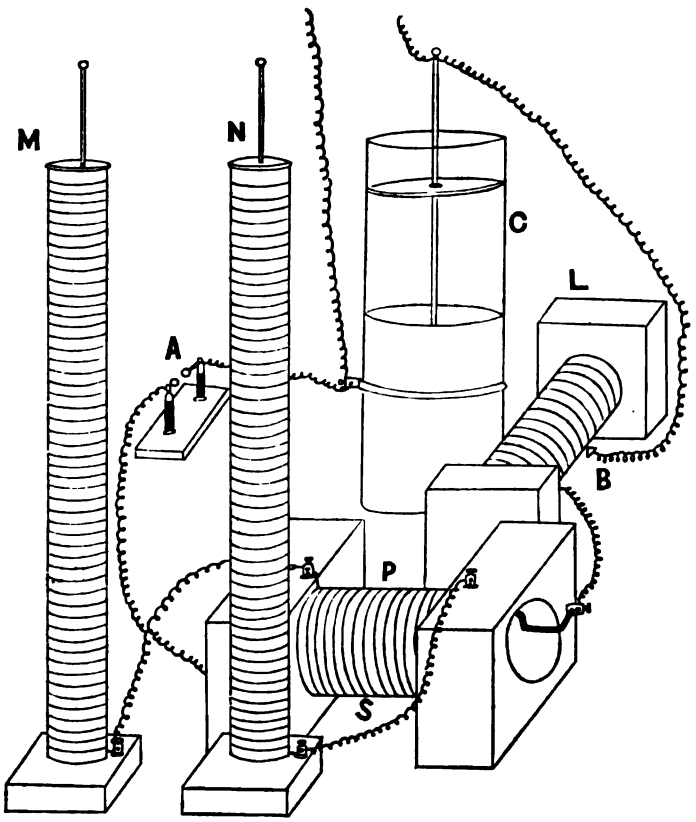


As shown in Fig. VI and Fig. VII, diagramactically and perspectively, the primary circuit consists of a principal coil *P*, an accessory adjustable one *L*, a spark-gap *A*, and a Leyden jar *C*. The coil *P* is placed in the interior of a hollow wooden coil, and on the external surface of the latter a number of turns of bare copper wire *S* are wound in a single layer. The coil *S* we may call an "impulse coil" for the reason to be described below. It is desirable to note that the coil *P* is removable and when necessary it can easily be replaced by another one, and also that the same statement applies to the Leyden jar *C*.

Now, if we attach to the terminals of the impulse coil a coil M or N, or both simultaneously in case the two coils have the

same electirical dimensions, powerful electric resonance can be established in these coils by properly adjusting the self-induction

Fig. VII.



of the coil *L*. Any coil, so to speak, when connected with one of the terminals of the coil *S* can be set in a state of resonance, and such phenomena relating to resonance coils, as described in my paper on resonance coils[1] can be observed with great ease. The stationary electric vibrations which take place in the coils are due to the electric impulse given to the coil *S* by the primary oscillations.

[1] The Electrician. Vol. 51, No. 16, Aug. 1903.

A Graphical Representation of Potential Drops and Distribution of Currents in a Network System.

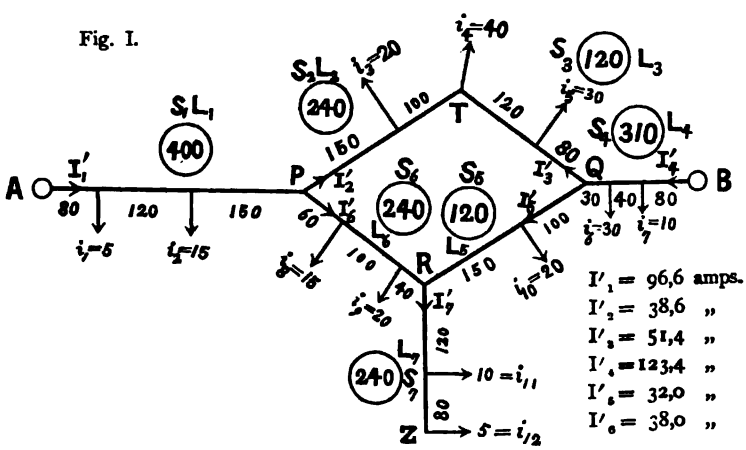
By

E. Aoyagi.

C. Hochenegg,[1] B. Soschinski[2] and G. König[3] have already treated some particular cases relating to this subject, but its general solution was not given by them. The aim of the author is to give a method for the general graphical solution of potential drops and distribution of currents in a network system; and also to show how drops and distribution of currents are affected by connecting or cutting off some conductors, or by increasing or decreasing loads at any points in the network.

The potential drops and distribution of currents in the direct-

Fig. I.



current network may be, of course, mathematically calculated

[1] Anordnung und Bemessung Elektrischer Leitungen.
[2] E. T. Z. p. 359. No. 17. 1902.
[3] E. T. Z. p. 69. No. 5. 1903.

by a well known method. In the network shown in Fig. I, A and B are two feeding-points, whose potentials are equal and always kept constant. Let $2\varepsilon_1$, $2\varepsilon_2$, $2\varepsilon_3$ and $2\varepsilon_4$ be the potential drops at the junction points P, Q, T and R; and let S and L be the sectional area in square mm., and the length in meters of the any side of the network, respectively. Then we have the following equations, from which ε may be evaluated at once:

$$\varepsilon_1\left(\frac{S_1}{L_1}+\frac{S_2}{L_2}+\frac{S_6}{L_6}\right)=\varepsilon_3\frac{S_2}{L_2}+\varepsilon_4\frac{S_6}{L_6}+\frac{1}{K}\sum_{L=1,2,6}\left\{\frac{\Sigma il}{L}\right\}, \text{ \&c. } (1),$$

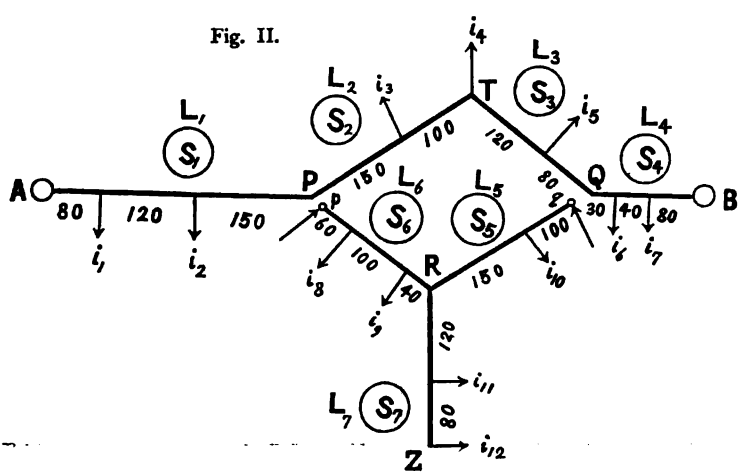
where K is the conductivity of a copper wiref 1 mm. square in the cross-section and 1 meter in length.

Again let $2\varepsilon_\alpha$ and $2\varepsilon_\beta$ be the potential drops at two ends of any side in the network and I_α, the current flowing out from the junction point α at one end. Then the current I_α is given by the following equation,

$$I_\alpha=(\varepsilon_\beta-\varepsilon_\alpha).K.\frac{S}{L}+\frac{\Sigma il}{L}. \quad . \quad . \quad (2).$$

The validity of the above equations (1) and (2) can be, o,

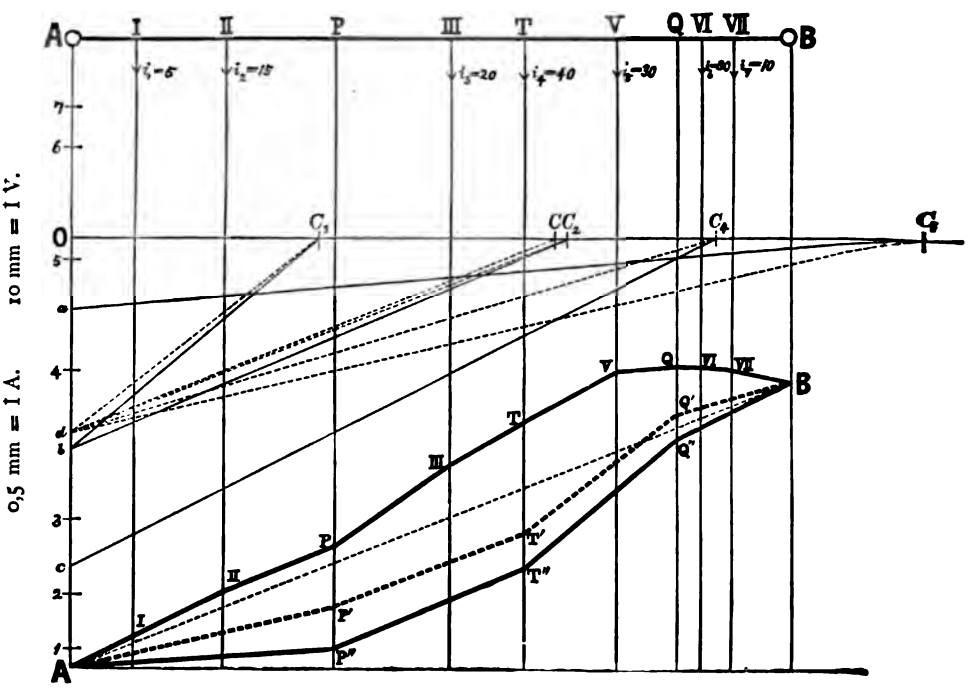
Fig. II.



course, established without difficulty. But the object of the author is to replace ordinary mathematical process by a method of graphical representation. This method affords us a means of vividly representing the electrical state in the whole network.

To take an example. Let the network be disconnected at P and Q as shown in Fig. II, and the detatched section be fed at its extremities p and q, whose potential drops are $2\,\varepsilon_p$ and $2\,\varepsilon_q$. Let the "current-branching lines" (Stromabzweigungslinien) for the upper and lower sections be respectively $APTQB$, $p\,R\,q$ and rXI XII (Fig. III and IV). To draw the "current-supplying line" (Stromzuführungslinie) for each of the sections under consideration, make use of the following equation

Fig. III.



0,5 mm = IA. 10 mml = IV.

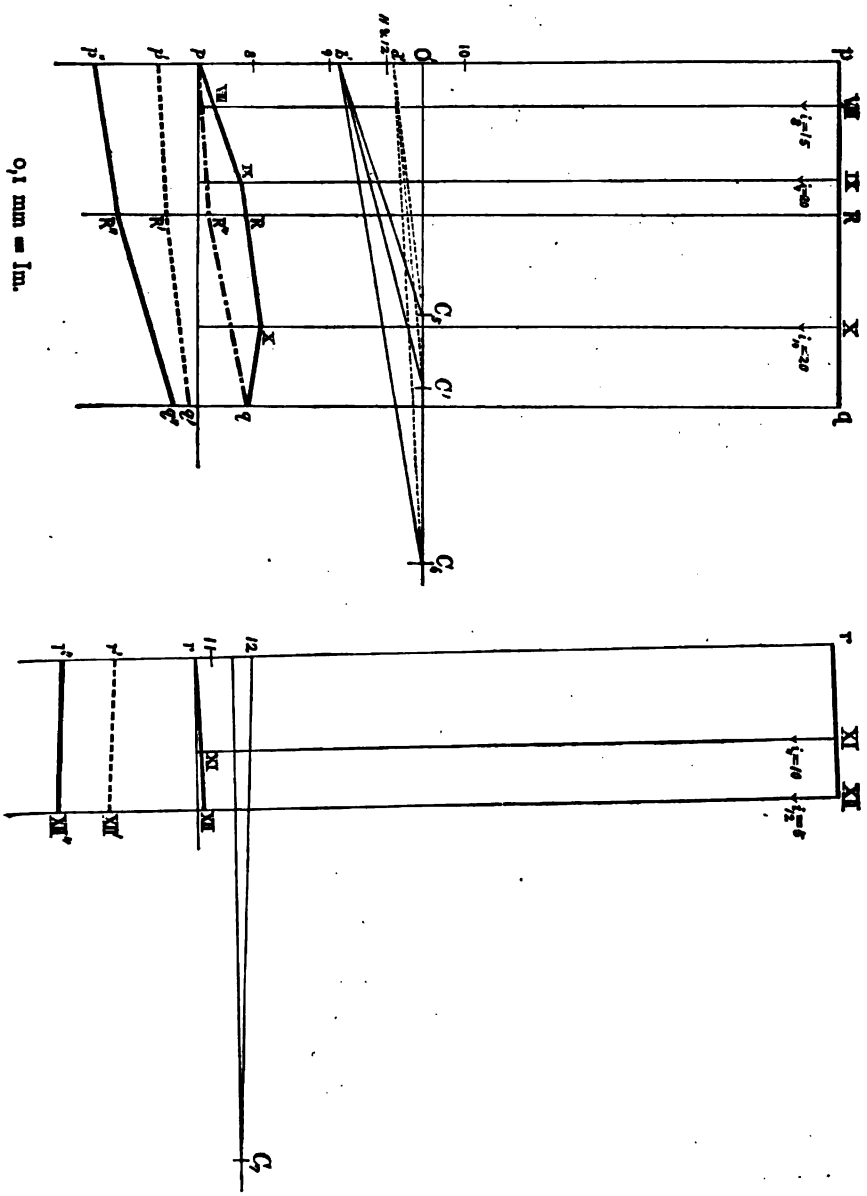


Fig. IV.

0,1 mm = Im.

$$\Sigma\, CC_x \frac{L_x}{S_x} = 0$$

$$\text{or } OC = \frac{K}{n} \cdot \frac{L}{\Sigma \frac{L_x}{S_x}} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and find the point C. The latter point being found, we have then to draw Cd parallel to the line AB, and the point d is then determined. Again draw AP', $P'T'$, $T'Q'$, and $Q'B$ parallel to $d\ C_1$, $d\ C_2$, $d\ C_3$ and $d\ C_4$, respectively. This gives us the "current-supplying line" $AP'-T'Q'B$. Taking $pp' = \varepsilon_p$, $qq' = \varepsilon_q$ and $rr' = RR'$, we get similarly the "current supplying lines" $p'R'q'$ and r' XII′ (Fig. IV).

It is to be noted that if p and q are the feeding-points, the "current-supplying line" would be $pR'''q$.

Now connect P and Q to p and q respectively. Then the potential drops and the distribution of currents will take quite a different aspect. Let $2\,y_1$, $2\,y_2$, $2\,y_3$ and $2\,y_4$ denote the increases of the potential drops at P, Q, T and R, respectively, as shown in Fig. III and IV. Then taking

$$\left.\begin{array}{l} P'P'' = y_1, \\ Q'Q'' = y_2, \\ T'T'' = y_3 \end{array}\right\} \text{(Fig. III)},$$

and

$$\left.\begin{array}{l} R'R'' = \varepsilon_4, \\ p'p'' = \varepsilon_P + y_1 - \varepsilon_p = m + y_1 \\ q'q'' = \varepsilon_Q + y_2 - \varepsilon_q = n + y_2, \\ r'r'' = \text{XII}'\text{XII}'' = R'R'' \end{array}\right\} \text{(Fig. IV)},$$

$$\text{where } \begin{array}{l} \varepsilon_P = PP', \\ \varepsilon_Q = QQ', \\ m = \varepsilon_P - \varepsilon_p, \\ n = \varepsilon_Q - \varepsilon_q. \end{array}$$

we get new "current-supplying lines" $AP''T''Q'B$, $p''R''q''$ and r XII."

For, draw $C_1 a$, $C_2 b$, $C_3 b$ and $C_4 c$ parallel to AP'', $P''T''$, $T''Q''$ and $Q''B$, respectively (Fig. III), and $C_6 b'$ and $C_5 b'$ parallel to $p''R''$ and $R''q''$, respectively (Fig. IV). Then we have

$$\left.\begin{aligned} I_1' &= Aa, \\ I_2' &= Ab, \\ I_3' &= 7b, \\ I_4' &= 7c, \\ I_5' &= bc, \\ I_6' &= ba, \end{aligned}\right\} \text{(Fig. I and III)},$$

and

$$\left.\begin{aligned} I_5' &= 10b' \\ I_6' &= p\,b' \end{aligned}\right\} \text{(Fig. IV)}.$$

Also we obtain

$$\frac{ad}{P'P''} = \frac{C_1 a}{AP''} = \frac{C_1 O}{L_1} = \frac{H_1}{L_1}, \text{ \&c.,}$$

$$\left.\begin{aligned} i.e.\quad ad &= \frac{H_1}{L_1} y_1, \\ bd &= \frac{H_2}{L_2}(y_1 - y_3) = \frac{H_3}{L_3}(y_3 - y_2), \\ cd &= \frac{H_4}{L_4} y_2, \\ b'd'' &= \frac{H_6}{L_6}(m + y_1 - y_4) = \frac{H_5}{L_5}\left\{y_4 - (n + y_2)\right\} \end{aligned}\right\} \text{(Fig. III and IV)} \quad \ldots (4)$$

$$\therefore \quad \left.\begin{aligned} ab &= ad + bd = \left(\frac{H_1}{L_1} + \frac{H_2}{L_2}\right) y_1 - \frac{H_2}{L_2} y_3, \\ bc &= cd - bd = \left(\frac{H_3}{L_3} + \frac{H_4}{L_4}\right) y_2 - \frac{H_3}{L_3} y_3, \\ pb' &= pd'' - b'd'' = I_6 + \frac{H_6}{L_6}\left\{y_4 - (m + y_1)\right\}, \\ 10b' &= 10d'' + b'd'' = I_5 + \frac{H_5}{L_5}\left(y_4 - (n + y_2)\right\} \end{aligned}\right\} \quad \ldots (5)$$

where $I_6 = p\,d''$

$I_5 = 10d''$.

In the above equations, since $ab=pb'$ and $bc=10b'$, we have

$$\left.\begin{aligned} y_1\left(\frac{H_1}{L_1}+\frac{H_2}{L_2}+\frac{H_6}{L_6}\right)&=y_3\frac{H_2}{L_2}+(y_4-m)\frac{H_6}{L_6}+I_6,\\ y_2\left(\frac{H_3}{L_3}+\frac{H_4}{L_4}+\frac{H_5}{L_5}\right)&=y_3\frac{H_3}{L_3}+(y_4-n)\frac{H_5}{L_5}+I_5\end{aligned}\right\}\quad .\ .\ (6)$$

i.e. since $H=KS$,

$$\left.\begin{aligned} y_1\left(\frac{S_1}{L_1}+\frac{S_2}{L_2}+\frac{S_6}{L_3}\right)&=y_3\frac{S_2}{L_2}+(y_4+\varepsilon_p-\varepsilon_P)\frac{S_6}{L_6}+\frac{I_6}{K}\\ y_2\left(\frac{S_3}{L_3}+\frac{S_4}{L_4}+\frac{S_5}{L_5}\right)&=y_3\frac{S_3}{L_3}+(y_4+\varepsilon_q-\varepsilon_Q)\frac{S_5}{L_5}+\frac{I_5}{K}\end{aligned}\right\}.\ (7),$$

where I_6 and I_5 express the currents supplied from p and q, before connecting the two sections of the given network.

If H is taken equal to $\frac{KS}{n}$, as usual, we should have $\frac{nI}{K}$ instead of $\frac{I}{K}$ in the above equations (7). Moreover we can derive the following two equations from (4),

$$\left.\begin{aligned} y_2\left(\frac{S_2}{L_2}+\frac{S_3}{L_3}\right)&=y_1\frac{S_2}{L_2}+y_2\frac{S_3}{L_3},\\ y_4\left(\frac{S_5}{L_5}+\frac{S_6}{L_6}\right)&=(y_1+\varepsilon_P-\varepsilon_p)\frac{S_6}{L_6}+(y_2+\varepsilon_Q-\varepsilon_q)\frac{L_5}{S_5}\end{aligned}\right\}.\ (8).$$

The quantities S, L, ε_P, ε_Q, ε_p ε_q, I and K being all known, we can find the values of the four unknown quantities y_1, y_2, y_3 and y_4 from the equations (7) and (8). Seidel's method[1] easily gives us the values of the above unknown quantitis, and therefore taking $P'P''=y_1$, &c, we obtain "current-supplying lines" $AP''T''Q''B$, $p''R''q''$ and r''XII." Then the potential drop at any point in the network will be represented by the intercept of the ordinate between the curves ATB and $AT''B$.

Thus, first cutting off any given network into a number of suitable sections, find graphically the potential drops and the distribution of currents, and then connecting them together into

[1] Teichmüller, Elektrische Leitungen p. 139.; Herzog-Feldmann, die Berechnung Elektrischer Leitungsnetze p. 285.

the original form, find the change of voltages and currents. This gives us the required potential drops and distribution of currents in the given network system.

So far, the discussion is quite general. However for practical application, we find it simpler, if it can be done, to take $\varepsilon_p = \varepsilon_P$ and $\varepsilon_q = \varepsilon_Q$.

It is here desirable to note that the correctness of the equations (7) and (8) can be proved by the aid of the equations (1) and (2).

In addition to the two feeding-points A and B, if we have another feeding-point Z, we obtain the following equations:

$$\left.\begin{aligned}
y_1\left(\frac{S_1}{L_1}+\frac{S_2}{L_2}+\frac{S_6}{L_6}\right) &= y_3\frac{S_2}{L_2}+(y_4+\varepsilon'_p-\varepsilon_P)\frac{S_6}{L_6},\\
y_2\left(\frac{S_3}{L_3}+\frac{S_4}{L_4}+\frac{S_5}{L_5}\right) &= y_3\frac{S_3}{L_3}+(y_4+\varepsilon_q'-\varepsilon_Q)\frac{S_5}{L_5},\\
y_3\left(\frac{S_2}{L_2}+\frac{S_3}{L_3}\right) &= y_1\frac{S_2}{L_2}+y_2\frac{S_3}{L_3},\\
y_4\left(\frac{S_5}{L_5}+\frac{S_6}{L_6}+\frac{S_7}{L_7}\right) &= (y_1+\varepsilon_P-\varepsilon_p')\frac{S_6}{L_6}+(y_2+\varepsilon_Q\\
&\quad -\varepsilon_q')\frac{S_5}{L_5}
\end{aligned}\right\} \quad .(9).$$

In order to get a clearer idea, let us consider the following example:

Suppose

$$\left.\begin{array}{ll}
i_1=5 \ \textit{Amp.} & i_7=10 \ \textit{Amp.}\\
i_2=15 \ ,, & i_8=15 \ ,,\\
i_3=20 \ ,, & i_9=20 \ ,,\\
i_4=40 \ ,, & i_{10}=20 \ ,,\\
i_5=30 \ ,, & i_{11}=10 \ ,,\\
i_6=30 \ ,, & i_{12}=5 \ ,,
\end{array}\right\},$$

and

$$\left.\begin{array}{ll}
S_1=400 \ mm^2 & S_5=120 \ mm^2\\
S_2=240 \ ,, & S_6=240 \ ,,\\
S_3=120 \ ,, & S_7=240 \ ,,\\
S_4=310 \ ,, &
\end{array}\right\}$$

Then we have

$$H_1 = \frac{1}{n} \cdot K.S, \text{ \&c,}$$

where $n = 20$,
$k = 55$.

i, e.

$$\left.\begin{array}{ll} H_1 = 110\ mm & H_5 = 33\ mm \\ H_2 = 66\ \ ,, & H_6 = 66\ \ ,, \\ H_3 = 33\ \ ,, & H_7 = 66\ \ ,, \\ H_4 = 85{,}5\ \ ,, & \end{array}\right\}.$$

Now in order to find the points C and C' and the increases of potential drops, we must calculate the values of $\Sigma \frac{L}{S}$ and $\Sigma \frac{S}{L}$, and the calculated values are given in the following tables:

Table (1)

Pole-distances	No. of sides	$\frac{L}{S}$	$\Sigma \frac{L}{S}$
$O\ C$	1 2 3 4	0,875 1,041 1,668 0,484	4,068
$O\ C'$	5 6	2,082 0,834	2,926

Table (2)

Increases of *P. D.*	No. of sides	$\frac{S}{L}$	$\Sigma \frac{S}{L}$
y_1	1 2 6	1,142 0,960 1,200	3,302
y_2	3 4 5	0,600 2,066 0,480	3,146
y_3	2 3	0,960 0,600	1,560
y_4	5 6	0,480 1,200	1,68

From the equation (3) and the table (1), we get

$$\left.\begin{array}{l} OC = 64{,}2\ mm \text{ (Fig. III)} \\ O'C' = 42{,}4\ mm \text{ (Fig. IV)} \end{array}\right\}.$$

Then we have

$$\varepsilon_P - \varepsilon_p = 8{,}1 - 5{,}0 = 3{,}1 mm$$
$$\varepsilon_Q - \varepsilon_q = 6{,}4 - 7{,}5 = -1{,}1\ \ ,,$$

where ε_P and ε_Q are graphically known from Fig. III.

Combining the equations (7) and (8) with the table (2), we obtain

$$\left.\begin{array}{l} y_1 \cdot 3{,}302 = y_2 \cdot 0{,}96 + y_4 \cdot 1{,}2 \ + 5{,}74 \\ y_2 \cdot 3{,}146 = y_3 \cdot 0{,}6 \ + y_4 \cdot 0{,}48 + 3{,}8 \\ y_3 \cdot 1{,}56 \ = y_1 \cdot 0{,}96 + y_2 \cdot 0{,}6 \\ y_4 \cdot 1{,}68 \ = y_1 \cdot 1{,}2 \ + y_2 \cdot 0{,}48 + 3{,}192 \end{array}\right\} \quad . \quad (10).$$

By making use of Seidel's method, we easily find

$$\left.\begin{array}{ll} y_1 = 3{,}77 & mm \\ y_2 = 2{,}29 & \,,, \\ y_3 = 3{,}16 & \,,, \\ y_4 = 3{,}09 & \,,, \end{array}\right\} .$$

Taking $P'P'' = 3{,}77$, &c., drawing the three "current-supplying lines" $AP'T''Q'B$, $p'R''q''$ and r'' XII'', and then drawing the parallel lines C_1a, C_2b, C_3b, C_4c, C_5b' and C_6b', the potential drop at any point and the current in any side of the given network are known at once.

To take an example, the potential drops at the points P, Q, T, R and Z, are

$$\left.\begin{array}{ll} 2\ \varepsilon'_P = 2{,}7 & Volt \\ 2\ \varepsilon'_Q = 1{,}9 & \,,, \\ 2\ \varepsilon'_T = 3{,}9 & \,,, \\ 2\ \varepsilon'_R = 3{,}4 & \,,, \\ 2\ \varepsilon'_Z = 3{,}8 & \,,, \end{array}\right\} ,$$

and the currents flowing out from the junction points A, B, P and Q, are

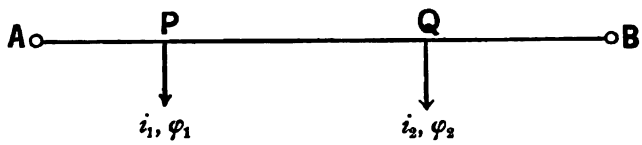
$$\left.\begin{array}{ll} I_1' = 96{,}6 & Amp. \\ I_2' = 38{,}6 & \,,, \\ I_3' = 51{,}4 & \,,, \\ I_4' = 123{,}4 & \,,, \\ I_5' = 32{,}0 & \,,, \\ I_6' = 38{,}0 & \,,, \end{array}\right\} .$$

In this case, since T and Z are the points with the maximum drop, their potential drops ought to be limited within an allowable value, namely, 2 % of the line voltage.

So far, we have concerned ourselves with a direct-current network.

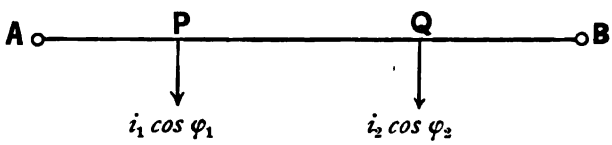
In the case of an alternating current network (Fig. V) whose self-induction is negligible, we have to consider separately the watt-current $i \cos \varphi$ and the wattless one $i \sin \varphi$ (Fig. VI and

Fig. V.



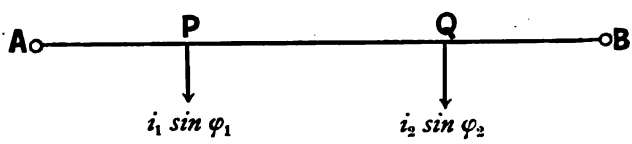
VII), φ being the phase angle by which the current i lags behind the *E.M.F.s.* impressed at the feeding-points A and B,

Fig. VI.



The network with watt-currents.

Fig. VII.



The network with wattless currents.

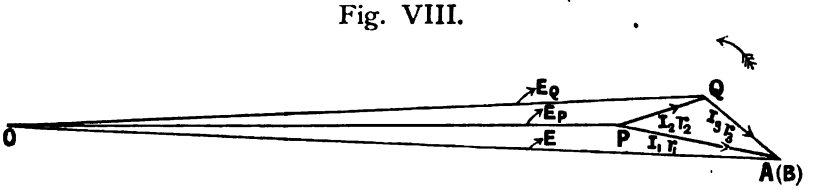
which are equal in magnitude and in phase with each other.

Now let us find graphically the potential drops and the distribution of currents in each of the above two cases, by means of the method which we have discussed at length in the case of a direct-current network. The resultant value of the current flowing in any side and that of the potential drop at any point are given by the hypothenuse of a right-angled triangle, described with the watt and wattless currents as the two sides in the first case, and with ohmic and inductive drops in the second case.

The exact mathematical determination of the value of φ is not easy. But in the distributing mains, the allowable maximum potential drop being less than about 2 % of the line voltage, we may practically take the phase angle between the impressed *E.M.F.* and the current of each load as the approximate value of φ.

Lastly, it is to be noted, that in the case of the alternating current network with both inductive and non-inductive loads, there takes place an interesting phenomenon. Under certain conditions, the currents flowing in some parts of the network may lead with respect to the impressed *E.M.F.* Suppose that *P* (Fig. VI) is the point with the maximum drop produced by the watt-currents and consequently it is also the point with the lowest voltage in the whole network. Again suppose that *Q* (Fig. VII) is the point with the maximum drop produced by the wattless currents, and consequently it is also the point whose impressed *E.M.F.* has the greatest phase angle leading with respect to the *E.M.F.s.* impressed at the feeding-points *A* and *B* (Fig. VIII). In the diagram (Fig. VIII), let I_1, I_2 and I_3, represent the currents in

Fig. VIII.



the three sections of the line, *i,e. AP, PQ* and *QB*, and *E*, E_P and E_Q, the *E.M.F.s.* at *A*, *i,e. B*, *P* and *Q*, respectively. Then, it is clear that the currents I_1 and I_3 lag behind the *E.M.F.s.*, while the current I_2 is in advance.

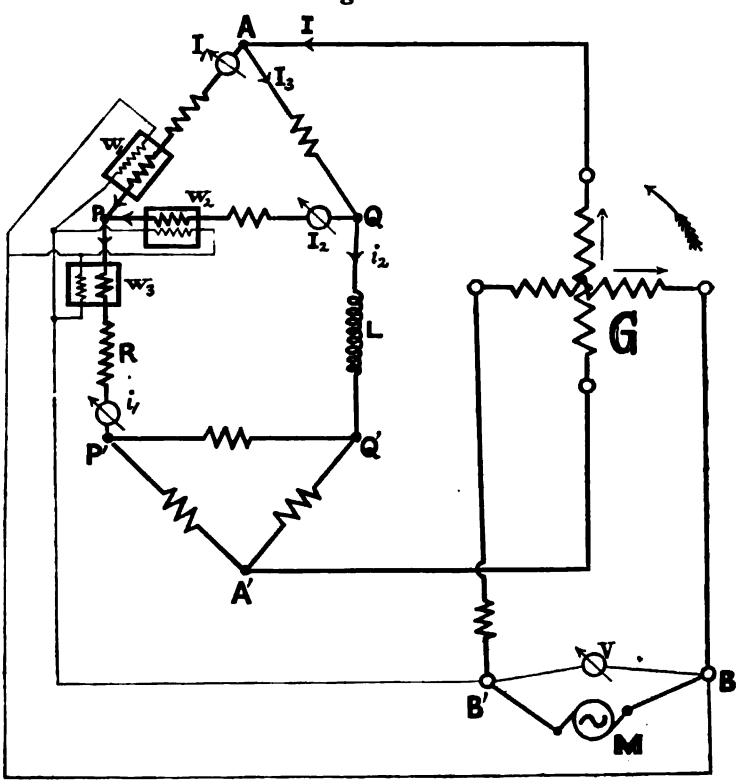
Thus decomposing the given loads into two, one of which is in phase with, the other at the right angle to, the impressed *E.M.F.s.*, and finding the points corresponding to the maximum drops and thereby the distribution of currents in the two cases, we see that those currents, whose watt and wattless consponents

take diagramatically opposite directions with each other, are in advance of, while the remaining currents, whose compoments have the same directions, are all in lag behind, the impressed *E.M.F.s.*

This phenomenon may be utilized in laboratories to produce leading currents without using any condensers or synchronous motors.

I will now describe an experiment, which confirms the above view. Let i_1 be the current in a non-inductive circuit composed of incandescent lamps, and i_2, that in an inductive circuit consisting

Fig. IX.



of coils (Fig. IX). The one-phase terminals of a two-phase generator *G* were connected with the feeding-points *A* and *A'*, and the other-phase terminals with a small synchronous motor *M*, the

latter being employed for the adjustment of the phase angle of the *E.M.F.* E' impressed between B and B' whose terminals were connected with each pressure coil of the wattmeters W_1, W_2 and W_3. The series coils of the latter were inserted in the branches AP, QP and PP'. Then the loads were adjusted so as to let P be the point with the maximum drop, and the phase angle of E' was adjusted by changing the excitation of the synchronous motor, until the deflection of the wattmeter W_3 indicated zero. In this state, the phase angle of the current i_1, which is in phase with E_P, differs by 90° from E'. Taking the readings of the other two wattmeters W_1 and W_2, we obtained the deflections of the needles in the opposite directions. This shows that I_1 was in lag behind E_P, while I_2 was in advance of it, as can be easily seen from the diagram (Fig. X). By meas-

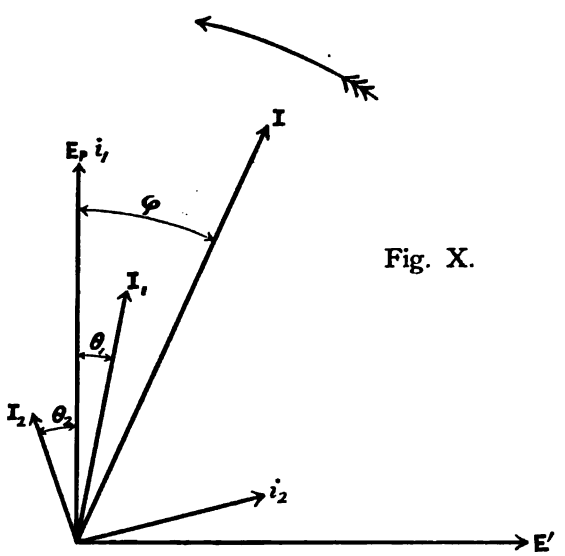


Fig. X.

uring I_1, I_2, E', W_1 and W_2, I determined the phase angles θ_1 and θ_2 (Fig. X). The results of the experiment are

$$\left.\begin{array}{l} I_1 = 6{,}8 \ Amp. \\ I_2 = 3{,}6 \quad ,, \end{array}\right\},$$

$$\left.\begin{array}{l} E'=109 \ \textit{Volt.} \\ E_Q=97{,}5 \ \ ,, \\ E_P=94{,}5 \ \ ,, \end{array}\right\},$$

$$\textit{and} \ \left.\begin{array}{l} E'I_1 \sin\theta_1=0{,}138 \ \textit{K. W.} \\ E'I_2 \sin\theta_2=-0{,}13 \ \ ,, \end{array}\right\}.$$

$$\therefore \ \left.\begin{array}{l} \theta_1= \ \ 10°44' \\ \theta_2=-19°22' \end{array}\right\},$$

and they are represented in the diagram (Fig. X).

It is here to be remarked that in the above experiment, I have used only one voltmeter, one amperemeter, one wattmeter and proper switches.

Defects of Uncarburetted Water-Gas as Fuel for Laboratory Use.

By

M. Chikashige and **H. Matsumoto.**

To those who have to find gas-fuel for their laboratories, water-gas will commend itself because of the little room taken up by the apparatus for making it, and from the relative simplicity of its manufacture and purification, owing to the fact that very little tar is produced. There will also be taken into account the comparatively small disadvantage of interrupting the manufacture to suit one's convenience, and of thus working the process intermittently.

Governed by such considerations as these, we have for several years endeavoured to make use of water-gas for ordinary purposes in our chemical laboratories, and principally in Bunsen burners. Being now convinced of its unfitness for this purpose, we offer an account of our results for the information of those who, like ourselves, have to provide their own gas-supply as well as of those who, though more fortunate, may find interest in the problem of the utilisation of water-gas.

Gas Used.

The gas which we made and used was analysed from time to time. Its average composition is given in the following table of volume percentages:—

Hydrogen	48.8
Methane	0.8
Carbon monoxide	33.1
Carbon dioxide with some hyd. sulphide	8.5
Nitrogen	8.5
Oxygen	0.3

The gas was purified only to the extent deemed sufficient and was supplied under a pressure of 5 cms. of water. The plant being set up very near to the laboratory, the iron main was very short, and therefore tarring the inside of it was neglected. Iron will consequently have been taken up in minute quantity by the carbon monoxide in the passing gas, and been present in it as iron carbonyl.

Burning of Water-Gas.

With the Bunsen lamp ready to hand as the almost universal laboratory gas-burner, we always used it for burning the water-gas, although the composition of this gas only allows the air-ways of a Bunsen burner to be opened to a small extent. In spite of the fact that the temperature of its flame is for most purposes rather too high, as will be shown presently, we cannot help admitting some air with the gas, because otherwise it will burn only in the outer border leaving the interior hollow and highly reducing.

Now the question which will present itself, as one not only of general interest but of practical importance in the use of this source of heat; is, what course is followed in the partial combustion of this mixture of gas and air,— does one of its combustible gases, hydrogen and carbon monoxide, burn before the other, or do they burn together? By slightly opening the air-valve of the burner, the usual two-coned flame is given by burning water-gas and we therefore burnt some of it in this way in a Smithells and Ingle's flame apparatus and analysed the gases between the two cones of the flame, obtaining results which, in the table that follows, are placed for comparison by the side of those published by Smithells and Ingle as obtained with coal-gas.

Partly burnt gas.	Water-gas. Vol. p. ct.	Coal-gas. (S. and I.) Vol. p. ct.
Water . . .	17.0	14.9
Hydrogen. . .	20.0	10.9
Methane . . .	0.3	trace

Carbon dioxide . .	8.8	3.8
Carbon monoxide .	19.5	10.2
Oxygen . . .	0.1	——
Nitrogen . . .	34.3	60.3

The numbers obtained with the water-gas show that about one volume of air had been mixed with two volumes of the gas, that being as much as could well be employed without risk of explosion. In Smithells and Ingle's experiments with coal-gas, nearly ten times as much air was used (9.6 to 2), but this difference is a matter of course and necessity. Two points of interest in the comparison are: (1) that in both cases the volume of the remaining hydrogen is about equal to that of the carbon monoxide, and (2) that the concentration of these gases is only half as great in the partly burnt coal-gas as it is in the partly burnt water-gas. Considered by itself, the result of the partial combustion of water-gas is of interest and importance as bringing out the fact that hydrogen burns before the carbon monoxide which is mixed with it. From this it follows that the inner cone of the flame of water-gas and air is that of burning hydrogen, and that in the outer cone of this flame and also in that of hydrocarbon flames the carbon monoxide must be the last constituent to burn.

Relative Value of the Water-Gas Flame.

We began this paper by stating some points in the manuacture of water-gas which seem to commend its employment in the laboratory in certain cases. But, as yet, we have made no mention of the advantage of using water-gas which arises out of the properties of its flame. Its advantageous properties when burning are, however, so well-known that we need not dwell upon them and we shall only refer to them, therefore, in order to point out the drawbacks which attend them. One advantage then is that the flame needs no air-draught to render it smokeless. Here, however, we often feel the want of the power at once to

reproduce the luminous, smoky flame of coal-gas, as when we have to ann.al in it glass which has just been worked.

Another advantage of this flame over that of coal-gas is afforded by its particularly high reducing power. Against this may be placed the comparative difficulty of using it for oxidising purposes. Only the outermost region and quite the tip of the visible flame can be thus used, whereas the Bunsen coal-gas flame acts oxidisingly to a considerable depth from its tip and surface. The reason of this difference may be found in the fact that, for fear of its flame passing down the tube, water-gas can be mixed with so little air from below, that the gas in the interior of the flame suffers very little combustion there. That, just as in a luminons coal-gas flame, the temperature inside the flame is much the lowest, can be easily demonstrated by holding a glass rod or a wooden splint across it.

One more property the flame possesses to its advantage is its high temperature. There is no ordinary gas-flame that in this respect equals it. In it comparatively thick copper wire and sheet, and even thin platinum wire are readily melted, and hard glass easily worked. Yet, it is just this property of specially high temperature which, along with the presence of so much carbon monoxide in the flame, makes its use often unsatisfactory, if not impracticable, for the ordinary work of the laboratory. This objection to the use of water-gas we shall now illustrate.

Insufficient Volume of the Flame.

With an equal flow of gas, the volume of the water-gas flame is much smaller than that of the coal-gas Bunsen flame. The reason of this lies largely in the fact that there is so much more to burn in the coal-gas and that its methane in burning to what is the analogue of water-gas, namely, carbon monoxide and hydrogen, or those two and water, besides the nitrogen of the consumed air, yields several times its volume of this combustible mixture. This fact of the small volume of the flame of water-gas seriously increases the necessary consumption of the

gas. For, when vessels of some size have to be heated, as is so often the case, the desirability of applying the heat over a wide extent of their surface can only be met by using a large enough flame, quite apart from any consideration of its temperature. In order to bring up the volume of the water-gas flame to that of the nonluminous coal-gas flame, it becomes necessary to increase the flow of the former to about two and a half times that of the latter. To give particulars: in an ordinary small Bunsen, such as we made use of, with its air-holes closed, and with a pressure on the gas (after passing through the meter) of 3 cms. water, 120 litres (nearly 4 ¼ cb. ft.) of gas will be consumed per hour and the length of the flame will be only 7 cms. or so; to get the ordinary Bunsen flame, that is, one about 15 cms. long, the aperture of the gas-nozzle must be enlarged until more than 300 litres (10 ⅔ cb. ft.) of the gas pass per hour. It will be evident that the much greater volume of water-gas required to give Bunsen flames of the ordinary size and also the effect of this requirement upon the capacity of the gas-plant show greatly to the disadvantage of water-gas when compared with coal-gas which, even in equal volumes, has much greater heat-giving power than water-gas. It must be remembered that in the routine of a teaching laboratory much gas is wasted, since everywhere the flame must be at hand even though not in use, because to that extent the relative heating power of the flame becomes a secondary point.

Copper Air-Baths and Water-Baths Rapidly Destroyed by the Flame.

Owing to the high temperature of the water-gas flame, a strip of sheet copper of considerable thickness not only melts in the flame, but, when held in the outer part of it, burns away quickly with bright scintillations. The edges of the flame have also a strongly oxidising action upon the bottoms of air-baths and water-baths and cause a constant stripping off of scales of black

oxide. In addition to this injury, these vessels suffer gradual destruction from the sulphur and the dust usually present in the gas, a point to be returned to later on. It becomes almost necessary, therefore, to replace copper water-baths by others of cast-iron, and to fit the copper air-baths with cast-iron bottoms, both of which stand fairly well.

Nickel and Platinum Vessels also Rapidly Destroyed.

Not only is copper so rapidly corroded, but rapid destruction of nickel and of platinum vessels is caused by the flame. In the case of these metals it is probably much less the high temperature of the flame than the presence in it of so large a proportion of carbon monoxide, that accounts for its injurious action upon them. We have had the bottom of a new nickel crucible burnt completely off in one operation, the metal being carbonised into a very brittle black substance. In what was perhaps the earliest attempt to construct an incandescence gas-mantle, Gillard found, in 1848, that a cage of platinum wire network suspended in a water-gas flame was soon corroded and then no longer incandesced brightly. In accordance with this observation, we have found that the bottoms of platinum dishes and crucibles get rapidly damaged by the flame, the metal becoming very brittle with a very white crystalline-looking surface. After continued use, a crucible of this metal has broken apart spontaneously, the metal when struck yielding no more sound than a piece of lead.

The experiment was made of heating a capsule formed out of platinum foil for many hours in the water-gas flame. One effect was a distinct though slight increase of weight. The metal became somewhat coated over by the heating, but this deposit was wiped off each time before weighing the capsule.

	Weight.
Before heating . .	4.7661 grms.
After 7 hours . .	4.7664 ,,
,, 5 ,, more .	4.7666 ,,
,, 10 ,, ,, .	4.7672 ,,

There was therefore a uniform increase of 1.1 part in 4766 parts. The increase in weight may have been due to the fixation of carbon or to the fixation of iron. As to the carbon it is to be remembered that Langer and V. Meyer in 1885 in their "Pyrochemical Researches" found carbon monoxide to suffer partial decomposition at 1690° into carbon and carbon dioxide. Not only is this the case, but we have found that carbon monoxide, hydrogen, and methane, mixed in the proportion occurring in water-gas, will sometimes deposit soot on the bottom of a porcelain crucible, although the flame is perfectly 'non-luminous'.

With regard to the iron, it is now an established fact that water-gas, which has passed some distance through bare iron pipes, contains iron carbonyl in the vaporous state, and from this iron carbide or iron oxide may be deposited on the platinum, or the platinum may take up iron. A platinum crucible which has been long heated by water-gas will be found to yield up traces of iron when treated with fusing potassium acid sulphate.

Even Porcelain Crucibles Unavailable for Use with the Flame in Quantitative Analysis.

A deposit, such as forms on the bottom of a platinum crucible, is also left upon the bottoms of porcelain crucibles heated in the water-gas flame, but in this case much of it is firmly adherent to the porcelain and cannot be wiped off. As a consequence the tare of the crucible is so affected as seriously to complicate the usual weighings, and indeed render accurate weighing impossible. The film thus formed is sometimes brown and consists then of iron oxides, silica, etc., but sometimes it is black and composed almost entirely of carbon and reduced iron, combined or not as carbide. The bottoms of three porcelain boats were kept for several days in the water-gas flame and became covered with this black deposit. After the increase in their weight had been ascertained, they were heated in a current of purified oxygen in a tube connected with a weighing tube containing crushed potassium

hydroxide. The increase in weight of the latter being attributed wholly to carbon dioxide, and the oxidised residue on the boats being assumed to be all ferric oxide, the black deposit proved to be a compound or mixture of iron and carbon, approximately expressed by $Fe\ C_2$:—

Deposit, 0.0097 grm.; carbon dioxide, 0.0117 grm.,= carbon, 0.0032 grm.; ferric oxide, 0.0100 grm.,=iron, 0.0070 grm. Carbon, 31.9 per cent.; iron, 68.6 per cent.

Theory: carbon, 30 per cent.; iron, 70 per cent.

The slight error in excess may perhaps have been due to the presence of a little hydrogen, miscalculated as carbon.

Deposition of a Dirty Pale-Blue Coating on Copper Vessels.

The action of water-gas flame upon the bottoms of copper vessels heated in it has already been noticed. Where the flame touches the copper, copper oxide is produced and scales off. But, besides this, all the copper above the edge of the flame which comes in contact with the hot products of combustion gets covered with a dirty bluish-white deposit which very easily detaches itself from the copper. It consists of nearly anhydrous copper sulphate with a little ferric oxide and traces of silica, magnesia, lime, etc. Now, such a deposit is known to be also produced by burning coal-gas, but in much less proportion, and in calling attention to this and other objections to the use of water-gas, we do not mean to convey the notion that there is any absolute difference between the burning of water-gas and coal-gas, but to point out the much greater prominence of its objectionable characters in the case of the water-gas. Killing in 1900 made an examination of a similar whitish deposit on the copper ceiling-protectors suspended over incandescence coal-gas burners and found it to consist largely of copper sulphate with other matters derived from the dust of the air and from the mantles. In the case of water-gas, particularly when used fresh from the generators, the impurities of the copper sulphate come

largely from the fine dust in the gas, as well as from iron carbonyl and silicon hydride. When the gas has not stood for some hours over water, its flame often has a reddish tinge.

Poisonous Character of Water-Gas.

The danger to health and life through the unrecognised escape of water-gas into the laboratory is well known. But even during the burning of the gas there may be danger. Lewes has pointed out that carbon monoxide in small quantities occurs among the gases from the flame of coal-gas and air of a Bunsen burner under a copper vessel, and Thorpe has recently determined its amount to be 0.022 vol. from 6 vols. of coal-gas. We have made some experiments with water-gas burnt under a sand tray and with a little air entering the Bunsen so as to form an inner cone in the flame. We worked according to Thorpe's method. For these experiments the water-gas was freed from hydrogen sulphide by passing it through a solution of lead acetate containing acetic acid, and was burnt at the rate of 170 litres (6. cb. ft.) per hour. When fully burnt, 100 vols. of the water-gas may be assumed to give 41 vols. of carbon dioxide.

The carbon monoxide escaping from the flame was found to vary greatly in quantity according to the position of the sand tray in the flame, as the following cases show :—

(1). With the tray some distance above the point of the inner cone, two experiments gave respectively 0.0010 gr. carbon monoxide to 0.1922 gr. carbon dioxide, and 0.0009 gr. to 0.1844 gr. The mean of these results comes out as 0.33 vol. carbon monoxide from every 100 vols. of water-gas burnt.

(2). When, on the other hand, the tray was placed below the point of the inner cone at about two-thirds of its height, there was a much greater escape of carbon monoxide. In this case, three experiments gave respectively 0.0028 gr. carbon monoxide to 0.1795 gr. carbon dioxide, 0.0028 gr. to 0.2149 gr., and 0.0032 gr. to 0.2241 gr. Calculation from these numbers brings

out the mean escape of carbon monoxide as 0.92 vol. to every 100 vols. of water-gas.

(3). Lastly, by working, as Lewes did, with the tray at the point of the inner cone, the three results obtained were 0.0016 gr. monoxide to 0.2170 gr. dioxide, 0.0015 gr. to 0.2009 gr., and 0.0015 gr. to 0.1907 gr., making a mean of 0.49 vol. of carbon monoxide to every 100 vols. of water-gas used.

The grand mean of these results is that 0.58 vol. of carbon monoxide escapes unburnt in the consumption of 100 vols. of water-gas in the usual ways, as described. This contrasts very unfavourably whith Thorpe's result with coal-gas, since 0.022 vol. from every 6 vols. of coal-gas burnt represents 0.37 per cent. Further, where work is done, as it usually is, with Bunsen flames of equal heights, when over 300 litres per hour of water-gas are burnt against 170 litres (6 cb. ft.) of coal-gas, the former contaminates the air with carbon monoxide nearly three times more than coal-gas, namely, to the extent of 1 vol. of carbon monoxide in place of the 0.37 vol. from coal-gas. The effect, therefore, is that where in a laboratory 30 coal-gas burners may be kept going without detriment to health, hardly 11 water-gas burners can be used with impunity.

For the reasons set forth in what precedes, we have been induced to give up the use of water-gas as a substitute for coal-gas in the laboratory.

On the Solubility of Gold-Silver Alloys in Potassium Cyanide Solutions.

By

J. Yokobori.

Since the discovery of the MacArthur Forest Process for the extraction of gold, the annual production of that metal has been enormously increased, and now the cyanide process obtains as the standard and most effective method in this branch of metallurgy. Many investigations, both theoretical and practical, have been caraied out by competent persons, and the results are giving great benefit to this comparatively new metallurgical process.

As is well known, gold and silver dissolve in potassium cyanide in the following manner :—

$$2Au + 4KCN + H_2O + O = 2AuK(CN)_2 + 2KOH.$$

$$2Ag + 4KCN + H_2O + O = 2AgK(CN)_2 + 2KOH.$$

The solubility of pure gold and pure silver, separately, in certain cyanide solutions has been experimentally established by certain authorities, but that of gold-silver alloys has remained entirely uninvestigated. Therefore it is my intention to investigate the solubility of these alloys in potassium cyanide solutions.

As every metallurgist knows, gold as it is found in its native condition, is not pure, but is always mixed with certain other materials, especially silver, as the following tables show :—

Fineness of Placer Gold.

	Gold	Silver
Aikawa, Sado . . .	585.1	—
Futsmi, „ . . .	597.5	—
Niibo, „ . . .	620.0	—
Nishimikawa, „ . .	666.6	—
Peichan, Hokkaido . .	792.3	192.9

Teshio, Japan . .	838.0	158.3
Usotannai, Japan . .	807.7	142.3
Yuhbari, „ . .	895.0	97.2
Sorachi, „ . .	843.0	—
Toimaki, „ . .	868.9	82.5
Shogawa, Hida. . .	838.3	157.1
Yoshinogawa, Iyo . .	903.9	—
Kiufun, Formosa . .	733.9	237.9
Irkutsk, Russia. . .	905.2	94.8
Tomsk, „ . . .	911.1	88.9
Barnaul, „ . . .	846.0	154.0
Corea	802.8	—
Chili	820.0	—
Queensland . . .	833.5	—
New South Wales . .	866.6	—
Victoria	908.9	—
Manchuria . . .	938.5	127.4
Transvaal . . .	836.4	133.6
California . . .	883.6	112.4
Colorado. . . .	820.5	175.5
Dakota	923.5	72.5
Georgia	922.8	73.2
Idaho	780.6	213.4
Montana	895.1	100.9
Oregon	872.7	123.3
Fineness of Mine Gold.		
Sado	565.8	—
Idsu	512.5	—
Kago	607.5	—
Yamagano . . .	635.7	—
Hoh	816.9	—
Ohkudzu. . . .	926.6	—
Ohtani	725.0	269.5
Ushio	720.8	227.8
Serigano	393.8	—

From these analyses, it will be seen that native gold, in whatever form it may occur, is not pure, but always contains some silver, the amount varying widely and ranging from 6 to 60%.

The behaviour of this impure gold in a potassium cyanide solution will surely be different from that in the case in which the pure metal only is considered, while for practical purposes it is more important to know the solubility of gold and silver alloys, in their varying compositions, in cyanide solutions than that of the pure metal.

Therefore, in my investigations, I have compounded gold-silver alloys of eleven different kinds, from pure gold to pure silver, each intermediate increase or decrease varying by 10% respectively, and these I have subjected to treatment in potassium cyanide solutions of different degrees of strength. The amount of alloy taken for the test samples was fifty grammes, the two elements being melted together in a muffle furnace, and afterwards rolled out into thin plates as is shown in Fig. I.

The alloy plates thus prepared were bored at the centre and suspended by horse hair in beakers each containing definite quantities of a known potassium cyanide solution. As free oxygen is necessary for the reaction of potassium cyanide on gold and silver, I blew into the cyanide solution in the beakers, a certain quantity of air once a day, with a hand bellows. When the reaction was finished, the metal residum in the beakers was taken out carefully, washed with clear water, then with alcohol, and last with ether. The dried residuum was then weighed very accurately, and afterwards remelted in cupels with the addition of some pure silver: then this new alloy was parted in order to obtain the pure gold alone. In this way the amounts of residual

gold and silver are readily determined, and then the quantity of those metals which has gone into solution may easily be calculated, either in quantity or in percentage.

The experiments were repeated five times, in different solutions, as is shown in the following tables:

I. Experiment.

No.	Alloy. gold. mgr.	Alloy. silver. mgr.	Potas. cyanide. 0.1%	Time. began	Residual gold. mgr.	Residual silver. mgr.	dissolved gold. %	dissolved silver. %
1	50	—	75c.c.	4P.M.	21.4	—	57.20	—
2	45	5	,,		21.0	0.2	53.30	96.00
3	40	10	,,	2 Nov.	21.3	4.3	46.75	57.00
4	35	15	,,		16.4	12.3	53.20	18.00
5	30	20	,,	ended	15.3	14.7	49.00	26.50
6	25	25	,,	4P.M.	13.6	13.0	45.60	48.00
7	20	30	,,		9.6	11.0	52.00	63.33
8	15	35	,,	6 Nov.	5.9	22.1	60.70	37.00
9	10	40	,,		9.6	18.2	4.00	55.50
10	5	45	,,		3.3	21.7	34.00	51.80
11	—	50	,,		—	28.9	—	42.20

II. Experiment.

No.	Alloy. gold. mgr.	Alloy. silver. mgr.	Potas. cyanide. 0.2%	Time. began	Residual gold. mgr.	Residual silver. mgr.	dissolved gold. %	dissolved silver. %
1	50	—	75c.c.	3P.M.	8.1	—	83.80	—
2	45	5	,,		10.3	1.4	77.11	72.00
3	40	10	,,	8Oct.	13.2	3.3	67.00	67.00
4	35	15	,,		9.3	4.6	73.43	69.33
5	30	20	,,	ended	8.2	5.8	72.67	71.00
6	25	25	,,	11A.M.	10.9	10.7	56.40	57.20
7	20	30	,,		9.0	14.2	55.00	52.67
8	15	35	,,	14Oct.	7.6	19.1	49.33	45.43
9	10	40	,,		5.0	20.4	50.00	49.00
10	5	46	,,		2.8	23.8	44.00	47.33
11	—	50	,,		—	17.2	—	65.60

III. Experiment.

No.	Alloy. gold. mgr.	Alloy. silver. mgr.	Potas. cyanide. 0.3%	Time. began	Residual gold. mgr.	Residual silver. mgr.	dissolved gold. %	dissolved silver. %
1	50.00	—	75c.c.		0.6	—	98.8	—
2	45.70	5.00	,,	3P.M.	3.8	0.8	91.7	84
3	40.40	10.00	,,	20.	6.5	2.0	83.9	80
4	35.20	15.00	,,	Oct.	4.6	2.6	86.9	82.7
5	30.00	20.00	,,		5.7	4.0	81.0	80.0
6	25.00	25.20	,,	ended	1.0	1.3	96.0	94.1
7	20.00	30.00	,,	2P.M.	0.4	1.5	92.5	95.0
8	15.00	35.40	,,	26.	1.3	5.2	91.3	85.6
9	10.00	46.40	,,	Oct.	2.1	10.8	79.0	76.7
10	5.00	45.80	,,		0.4	6.2	92.0	86.8
11	—	50.60	,,		—	16.4	—	67.6

IV. Experiment.

No.	Alloy. gold. mgr.	Alloy. silver. mgr.	Potas. cyanide. 0.4%	Time. began	Residual gold. mgr.	Residual silver. mgr.	dissolved gold. %	dissolved silver. %
1	50	—	75c.c.	4P.M.	14.0	—	72.00	—
2	45	5	,,	2Nov.	20.4	—	54.70	40.00
3	40	10	,,		17.4	4.8	56.50	52.00
4	45	15	,,		19.3	7.9	44.90	47.30
5	30	20	,,	ended	—	—	—	—
6	25	25	,,	3P.M.	2.4	7.4	90.40	70.40
7	20	30	,,	6Nov.	11.5	14.7	42.50	51.00
8	15	35	,,		6.4	17.2	57.30	50.90
9	10	40	,,		5.5	21.9	45.00	45.30
10	5	45	,,		3.3	23.1	34.00	59.80
11	—	50	,,		—	17.7	—	64.80

V. Experiment.

No.	Alloy. gold. mgr.	Alloy. silver. mgr	Potas. cyanide. 0.5%	Time. began	Residual gold. mgr.	Residual silver. mgr.	dissolved gold. %	dissolved silver. %
1	50	—	100c.c.		6.9	—	86.20	—
2	45	5	,,		undet.	undet.	—	—
3	40	10	,,		12.2	3.8	69.50	38.00

4	35	15	„	24	13.3	5.6	62.00	62.70
5	30	20	„		5.7	3.7	81.00	75.40
6	25	25	„	hours.	—	—	—	—
7	20	30	„		10.1	15.6	49.50	48.00
8	10	40	„		4.4	18.5	56.00	53.80
9	—	50	„		—	18.7	—	62.60

From the results of these experiments, it will be seen that the degree of solubility of pure gold and pure silver, together with their alloys, differs greatly with the concentration of the cyanide solution. In the weaker solutions, e. g. 0.1% or 0.2%, the gold and silver dissolve without regularity except that in experiment II. the solubility of gold decreases gradually with the increase of silver, and similarly, that of silver too with the decrease of gold. In solutions stronger than 0.3%, we see the solubility both of gold and of silver and of their alloys is nearly at the maximum when the component parts of gold and silver are equal in amount. This fact may be very interesting, if it can be firmly established by further investigation, although I am not yet in a position to insist upon these experimental results as general truths, still I believe these results will at least attract the attention of metallurgists who are interested in the extraction of gold by the cyanide process, and be productive of valuble results.

In addition to the above described experiments, I have tried to determine the effect of Zinc shavings upon certain potassium cyanide solutions, since they have great influence upon the economical treatment of gold-bearing ores. For this purpose I put 5 grammes of Zinc shavings into beakers of about 300–400c.c. capacity, poured over them 100c.c. of potassium cyanide solution of different degrees of concentration, and after an interval of 24 hours the strength of the solutions was determined.

I. Experiment.

No.	KCN Solution. 0.216%	Zinc Shaving.	Strength after24h.	Strength after48h.
1	100c.c.	5gr.	0.164%	0.08%
2	„	„	0.164%	0.136%

3	„	„	0.163	0.106
4	„	no Zinc	0.210	0.202

II. Experiment.

No.	KCN Solution. 0.3%	Zinc Shaving.	Strength after24h.	Strength after48h.
1	100c.c.	5gr.	0.228%	0.112%
2	„	„	0.230	0.170
3	„	„	0.230	0.180
4	„	no Zinc	0.290	0.274

III. Experiment.

No.	KCN Solution. 0.1%	Zinc Shaving.	Strength after24h.	Strength after48h.
1	100c.c.	5gr.	0.077%	0.072%
2	„	„	0.070	—
3	„	„	0.076	0.064
4	„	no Zince	0.096	0.092

On the Allanite Crystal from Hiei Mountain.

By

T. Hiki.

In this memoir I propose to give a brief description of a mineral called allanite, which forms an accessory ingredient of the biotite-granite, which extends over about four square kilometres on the south side of Hiei mountain. But beyond the above mentioned area, the rock reappears, with the same natural characteristics, and apparently forms a chain connecting Miyoken and Rokko mountains in the province of Settsu, and covers about one-half the area of the province of Awaji. In the said regions, the mineral is not always to be observed, excepting that which occurs microscopically in the province of Awaji, previously determined by T. Ogawa, of the Geological Survey.

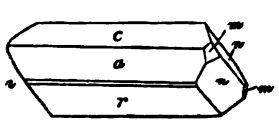
These intrusive masses of rock pierce through the Chichibu Paleozoic formation consisting of clay slate, greywacke-sandstone, hornstone, etc., and give contact metamorphism to these rocks.

I shall now proceed to describe some details of the rock and of the crystal.

The biotite-granite here mentioned is the ordinary light-colored, coarse-granular, fresh holocrystalline variety, composed of orthoclase, biotite, and quartz, as essentials, and a few other minerals as accessories. Orthoclose is the most predominant, but is almost always decomposed, more or less idiomorphic sodium felspar is also present, determined under the microscope by its characteristic polysynthetic sutures. Xenomorphic, angular quartz occurs, traversed by many cracks and liquid inclosures, which are common to all granites. Brown-colored biotite, with intense pleochroism, is

present, partially altered into green lamellæ by bleaching action. Dark-green hornblende occurs very sparsely on Hiei; while it is met with so abundantly in other places that the rock may be described as hornblende-biotite-granite.

The allanite crystal, not yet observed macroscopically in our country, is the most predominant accessory component of the Hiei granite: it was first discovered by me about five years ago at the granite quarry on Daimonji-mountain in the south-western corner of the granite mass. Thereafter, research on the distribution of that mineral was prosecuted by K. Yamada and myself, and at last we reached at the conclusion that the mineral is intimately dispersed throughout the mass. The crystal is a columnar, fresh mineral, raven-black in color, and has a vitreous lustre; is always isolated and is a perfectly well-defined crystal of epidote habitus. It is separated with difficulty from fresh rock, but, on the other hand, rather easily obtained from rock that is decomposed, and in the latter case the mineral is more or less affected by alteration, being coated with a brown film. The crystal habitus of the mineral is prismatic, elongated on the orthoaxis, flattened in the orthopinacoid direction, frequently terminated in both ends, and in large specimens, the size is 1cm. in length and 1mm. in breadth.



c=oP.
a=∞ P$\bar{\infty}$.
r=P$\bar{\infty}$.
n=P.

The crystalline form being quite simple, only the following faces are observed. The observed angles between the faces are as follows, the faces being uneven, however, a more accurate measurement was not possible with the available materials:

	Naumann	Rough measurement by Reflection Goniometer.	Rough measurement by Contact Goniometer.
ac	64° 59′	65° 16′	
ar	128° 18′	128° 24′	
nn	70° 52′		70° 0′

Of the faces, *c*, *a*, and *r* are prominent; while *n* is always rather small. In other specimens the face *l* ($2P\bar{\infty}$) truncates the faces *a* and *r* in a narrow band, and *m* (∞P) replaces the solid angle *nac*; their facial angles, also, could not be measured on account of the small faces.

Complete chemical analysis has not been conducted, but the reaction of cerium was obtained in the qualitative test.

Among its characteristics, it is to be noted that thin sections of the mineral are traversed by irregular cracks, enclosing abundant apatite needles in an orderless manner. These apatite needles, however, can hardly be designated as a grantitic component.

The pleochroism is very strongly marked. The axial colors observed are; a greenish-brown; b reddish-brown; and c brownish-yellow. Green epidote frequently intercalates without any definite arrangement. The zonal structure, which is common in many similar occurences, is almost entirely wanting.

Deflection and Vibration Diagrams of Kinokawa Railway Bridge Truss.

By

S. Tanabe.

The Kinokawa bridge near Wakayama, on the Nankwai railway company's line, consists of three 203′ 9″ span trusses, as shown in the annexed figure, with nineteen 70′ plate girders, built upon masonry and brick piers.

An experiment was made by the author on March 16th, 1903, when there was a trial run of a train over the bridge, to determine the deflection and vibrations of one of the trusses.

A vibration recorder, designed by the author, was laid upon a stable scaffolding just underneath the central pin of the truss, as is shown by the point O, of the figure.

The recorder consists of a revolving and shifting, smoked drum, 5¾″ in diameter and 4¾″ long, laid horizontally, with its axis parallel to the axis of the bridge. An arm with recording index was placed just underneath the point O, the central pin, and so arranged as to have the vertical deflection and the vertical vibrations magnified two times. The horizontal vibrations in the direction at right angles to the axis of the bridge are recorded with the exaggeration of 2.8 times. For position index of the load system, three electric checks were placed; one at the centre of the truss, one at 100 feet to the right, and one at 100 feet to the left of the centre of the truss.

When the forward leading-wheel of the locomotive pushes down the first check, mark A. is made on the drum; on coming to the centre of the span, mark B. is made; and similarly mark C. is made, the index being moved by magnet, an electric circuit

being closed by the contact of the check and the rail when leading-wheel of the locomotive pushes down the check. represents the position when all wheels of the train have passed over the truss. At one side of the recording drum tuning-fork driven electrically making and recording 31.6 vibra per second, was placed. In the figure, however, only every t vibration is marked in the central part of it.

The bridge is made of steel and is suited to a single lin railway of 3′ 6″ gauge. The span, from centre to centre of pins, is 203′ 9″, and the width, from centre to centre of trus is 16′ 2″. Heights are shown in the figure. Weights, per of the locomotive and the cars, are shown in tons, hund weights, and quarters.

Maximum deflection, of 11/16 inch, occured in the middle the truss, when the leading-wheel of the locomotive came to point M of the fourth panel; maximum vibration was 3/32 i with period of 1/4 second, while maximum horizontal vibra was 13/64 inch, with 0.8 second period, and occured when leading-wheel of the locomotive had just passed over the brid Minor vertical vibrations were felt a little before the train ca upon the truss: while minor horizontal vibrations were felt lo after the train had passed over. Movement of the bridge tr in direction of centre line of railway, being exceedingly sma can not be shown in the figure.

Note on the Body of Awata Pottery.

By

H. Matsumoto.

I was incited to make more extended research by the communication of the results obtained in the investigation, in 1898, by S. Matsunaga,[1] concerning a glaze which appears on the Awata body without "shivering" or "crazing." His conclusion was that the body of Awata pottery contains insufficient uncombined silica to bear a glaze without crazing. That body is composed of four clays: Shigaraki, Majeko, Shiraye, Mitsuishi. It is baked at a temperature sufficient to melt a Seger cone 020–022. The biscuit is covered with a glaze composed of Amakusa stone and the ash of the plant Distylium racemosum. It is then baked a second time to melt the glaze upon it, the heat reached being that of the melting-point of cone 7. The finished piece has a light straw colour; the glaze is minutely crazed; and the body is a porous, non-transparent mass, but it cannot be scratched with a knife.

Now, an attempt should be made to find a body which will bear the glaze of Awata pottery without crazing or shivering. For this purpose, I have, of necessity, been compelled to select the four clays mentioned above and a flint from Hinooka, as raw materials for producing the body; and first it was essential to analyse the component materials in order to arrive at an exact knowledge of their character.

Shigaraki clay, having been washed at the mine, is again sifted through a sieve covered with silk bolting-cloth, having 60

[1] Journ. Chem. Ind., Tōkyō, I., 9.

meshes in 1 linear cm. In this washing, 30% of residuum is held back by the sieve. This washed product is moderately plastic and has a grayish-yellow tint. A part of it was dried at 120° for preparation of the sample for a rational and total analysis: it has the following composition:

The entire clay contains%		Rational analysis.	
Silica	58.82	Clay substances	63.13
Alumina	27.13	Quartz	12.19
Ferric oxide	1.00	Felspathic detritus	24.68
Lime	0.88		
Magnesia	0.08		
Soda	1.28		
Potash	2.36		
Ignition loss	7.89		
Sum	99.44		

Shiraye clay is a low plastic, white clay. Being also subjected to the same elutriation, it leaves 16% residuum on the sieve: its composition is as follows:

The entire clay contains%		Rational analysis.	
Silica	47.51	Clay substances	97.05
Alumina	38.30	Quartz	1.22
Ferric oxide	0.57	Felspathic detritus	1.73
Lime	trace		
Magnesia	0.09		
Soda	0.19		
Potash	0.10		
Ignition loss	13.75		
Sum	100.51		

Majeko, being a sandy clay, only 30% of it passed through the sieve. The washed product has a white colour, and is rather a plastic clay. Its composition is as follows:

The entire clay contains%		Rational analysis.	
Silica	48.05	Clay substances	90.83
Alumina	37.26	Quartz	5.58
Ferric oxide	0.67	Felspathic detritus	3.60

Lime	0.25	(Continued).
Magnesia	0.10	
Soda	0.57	
Potash	1.14	
Ignition loss	12.28	
Sum	100.32	

Mitsuishi is a clay-stone which is pulverized before being sent to market. Its composition is as follows:

The entire clay contains%		Portion insoluble in H_2SO_4 and NaOH contains:	
Silica	56.72	Silica	37.87
Alumina	35.62	Alumina } Ferric oxide }	15.22
Ferric oxide	0.30		
Lime	0.71	Rest	0.11
Magnesia	0.06		
Soda	0.15		
Potash	0.26		
Ignition loss	7.63		
Sum	101.45		53.20

As this result shows, the portion of Mitsuishi clay which is insoluble in sulphuric acid and caustic soda, as compared with the felspar, has a higher content of alumina and a very small quantity of alkali; a composition which distinguishes it essentially from that part of the clays mentioned before. Thus the character of the mineral fragments being undefinable, its influence upon the pottery body is unknown, so that it seems better to reject the claystone as a raw material.

A native flint from Hinooka, which is ground for pottery purposes, has the following composition:

Silica	98.20
Total impurities	1.80

From these materials, trial pieces are made thus: after the quantity of clay in a definite volume of slip has been weighed, in order to get different mixtures, the slips are mixed in a mortar and then that mixed slip is readily thickened by pouring

it on a dry slab of plaster of Paris, and then moulded into plates. When the pieces are bone-dry, they are placed in a muffle and baked at the heat required to melt cone 020–022. The fired pieces are covered on one side with the glaze of the Awata pottery.

The composition of that glaze is as follows:

Silica	53.00	
Alumina	11.11	Chemical formula of the glaze:
Iron oxide	1.41	$\left.\begin{matrix}0.78\ CaO \\ 0.02\ MgO \\ 0.08\ K_2O \\ 0.12\ Na_2O\end{matrix}\right\}\left\{\begin{matrix}0.33\ Al_2O_3 \\ 0.03\ Fe_2O_3\end{matrix}\right\}2.68\ SiO_2$
Lime	14.24	
Magnesia	0.30	
Soda	2.53	
Potash	2.32	
Ignition loss	14.77	
Sum	99.68	

Then they are baked at the temperature at which cone 7 melts.

At first, taking Shigaraki clay as the basis, flint is added in the proportion of 1/8, 1/4, 3/8, 1/2 of the clay. Though the last three mixtures bear the glaze without crazing, they are, as compared with the original Awata body, too dense, as they are like a stoneware body and have a grayish tint. In order to improve the colour and to reduce the hardness, 2 parts of Shigaraki clay and 1 part of Majeko clay are mixed, and to this mixture 1/2, 1, 3/2, 2 parts of flint are added. The glaze holds good upon the last two mixtures, which are, however, still too hard and have a dirty yellow colour. Now 2 parts of Majeko clay and 1 part of Shigaraki clay are mixed, and to the mixture 1/2, 1, 3/2, 2, 5/2, 3 parts of flint are added. The last two mixtures bear the glaze without crazing or shivering; have a moderate hardness, and show a light straw colour: but their plasticity is practically insufficient to permit of fashioning them. All other attempts to get suitable body are failures. The following table, I., gives the ratios of the materials taken, and the constituent minerals, as well as the characteristics of the finished pieces:

TABLE I.

Ratio of the materials used.				Percentage composition of the component minerals.			Characteristics of the finished plate.	
Clay Shigaraki.	Clay Majeko.	Clay Shiraye.	Flint Hinooka.	Felspar.	Quartz.	Kaolin.	Body.	Glaze.
1				24.68	12.19	63.13	Hard, light yellowish gray.	Fine crazing.
1			1/8	21.94	21.74	56.32	Ditto.	Coarse crazing.
1			1/4	19.74	29.37	50.87	Ditto.	No crazing.
1	1/2			18.31	9.33	72.36	Ditto.	Fine crazing.
1			3/8	17.95	35.65	46.40	Ditto.	No crazing.
1			1/2	16.45	40.86	42.69	Ditto.	Ditto.
1	1/2		1/4	15.70	22.02	62.28	Ditto.	Coarse crazing.
1	1			15.13	7.90	76.97	Ditto.	Fine crazing.
1	1/2		1/2	13.73	31.55	54.72	Hard, straw colour.	Few crazing.
1	1/2		3/4	12.21	38.95	48.84	Ditto.	No crazing.
1	2			11.95	6.46	81.59	Ditto.	Fine crazing.
1		2/3	8/15	11.74	29.72	58.54	Moderate, straw colour.	Few crazing.
1	1/2		1	10.99	44.87	44.14	Ditto.	No crazing.

TABLE I (Continued).

Ratio of the materials used.				Percentage composition of the component minerals.			Characteristics of the finished plate.	
Clay Shigaraki.	Clay Majeko.	Clay Shiraye.	Flint Hinooka.	Felspar.	Quartz.	Kaolin.	Body.	Glaze.
1	1	1		10.66	5.67	83.67	Moderate, light straw colour.	Fine crazing.
1	2		1/2	10.24	19.57	70.19	Moderate, straw colour.	Coarse crazing.
1	1	1	3/10	9.69	14.08	76.23	Moderate, light straw colour.	Fine crazing.
1	2		1	8.96	29.40	61.64	Moderate, straw colour.	Coarse crazing.
1	1	1	3/5	8.88	21.08	70.04	Moderate, light straw colour.	Fine crazing.
1	1	1	9/10	8.21	27.02	64.77	Ditto.	Ditto.
1	2		3/2	7.97	37.04	54.99	Moderate, straw colour.	Coarse crazing.
1	1	1	6/5	7.61	32.11	60.28	Moderate, light straw colour.	Ditto.
1	2		2	7.17	43.16	49.67	Moderate, straw colour.	Few crazing.
1	1	1	3/2	7.11	36.51	56.38	Moderate, light straw colour.	Coarse crazing.
1	2		5/2	6.52	48.16	45.32	Ditto.	No crazing.
1	1	1	2	6.40	42.68	50.92	Soft, white.	Coarse crazing.
1	2		3	5.97	52.33	41.70	Soft, light straw colour.	No crazing.

TABLE I (Continued).

Ratio of the Materials used.				Percentage composition of the component minerals.			Characteristics of the finished plate.	
Clay Shigaraki.	Clay Majeko.	Clay Shiraye.	Flint Hinooka.	Felspar.	Quartz.	Kaolin.	Body.	Glaze.
1	1	1	5/2	5.82	47.73	46.45	Soft, white.	Coarse crazing.
1	1	1	3	5.33	51.94	42.73	Ditto.	Few crazing.
	1		1/3	4.19	27.25	68.56	Soft, light straw colour.	Coarse crazing.
	1	1		3.66	2.41	93.93	Soft, white.	Fine crazing.
	1	1	1/2	2.92	21.57	75.51	Ditto.	Coarse crazing.
	1	2	1/4	2.78	9.41	87.81	Ditto.	Ditto.
	1	2	1/2	2.58	15.76	81.66	Ditto.	Few crazing.
	1	1	1	2.44	34.34	63.22	Ditto.	Ditto.
	1	1	3/2	2.09	43.46	54.45	Ditto.	Ditto.
	1	2	1.9	1.85	39.30	58.85	Ditto.	Ditto.
	1	1	2	1.83	50.30	47.87	Ditto.	Ditto.

"Soft" means that degree of hardness in the body which barely admits of its being cut with a knife.

"Moderate" means that the steel leaves a lead-pencil-like mark on it, yet it is porous, and adheres when touched to the tongue.

"Hard" means that though it does not adhere to the tongue, yet it is non-transparent and infusible.

These results show, however, that the bodys which are fit for the glaze contain felspar and quartz in the following proportion :

For 20%–12% of felspar, more than 30%–40% of quartz.
„ 12%– 6% „ „ , „ „ 40%–50% „ „ .

But they are not suited to the finer products of the ceramic art, on account of their unsatisfactory colour and because of thier want of plasticity. Thus it becomes evident that, under the existing and ordinary conditions of the Awata ceramic manufacture, a satisfactory body which will bear the glaze without crazing or shivering, cannot be obtained from the available materials, even by the addition of quartz powder.

Hence, it becomes necessary to modify the process of the trials, in order to get a satisfactory ware. For this purpose the cakes are exposed to a higher temperature than at which the glaze runs bright, as in the prevailing process at the ordinary faience manufactories. When the firing of the biscuit kiln is continued until cone 11 has melted down completely, the clay pieces which contain more than 12% of felspar become too dense to take up water and the solids are washed off on withdrawal of the pieces from the creamy liquid of the glaze material. Biscuit of the proper condition, after being immersed in the slip of the glaze, are finished at the temperature of the ordinary Awata kiln. They have the characteristics enumerated in the following table II :

TABLE II.

Percentage composition of the component minerals.			Characteristics of the biscuit.	Characterisctics of the finished plate.
Felspar.	Quartz.	Kaolin.		
11.74	29.72	58.54	Moderate, straw colour.	No crazing.
10.99	44.87	44.14	Ditto.	Ditto.
10.66	5.67	83.67	Moderate, light straw colour.	Coarse crazing.
9.69	14.08	76.23	Ditto.	Ditto.

TABLE II (Continued).

Percentage composition of the component minerals.			Characteristics of the biscuit.	Characteristics of the finished plate.
Felspar.	Quartz.	Kaolin.		
8.88	21.08	70.04	Moderate, light straw colour.	Few crazing.
8.21	27.02	64.77	Ditto.	No crazing.
7.61	32.11	60.28	Ditto.	Ditto.
7.11	36.51	56.38	Ditto.	Ditto.
6.40	42.68	50.92	Ditto.	Ditto.
5.82	47.73	46.45	Ditto.	Shivering.
5.33	51.94	42.73	Ditto.	Ditto.
4.19	27.25	68.56	Soft, white.	No crazing.
2.92	21.57	75.51	Ditto.	Ditto.
2.78	9.41	87.81	Ditto.	Ditto.
2.58	15.76	81.66	Ditto.	Ditto.
2.44	34.34	63.22	Ditto.	Shivering.
2.09	43.46	54.45	Ditto.	Ditto.
1.85	39.30	58.85	Ditto.	Ditto.
1.83	50.30	47.87	Ditto.	Ditto.

From an inspection of the table it appears that the bodys which contain every 1 part of three clays and 9/10 to 3/2 parts of flint, or 56.38 to 64.77 Kaolin, 7.11 to 8.21 felspar, and 36.51 to 27.02 quartz, carry the glaze nicely, and are free from crazing, have a light straw colour and are moderately hard. They are also susceptible of being fashioned.

The relative proportions of quartz for felspar of those bodys which carry the glaze without crazing and shivering, leaving plasticity, colour and hardness out of consideration, are as follows:

[illegible]

[illegible] manner that [illegible] the available [illegible] are [illegible] that if they [illegible] in fashioning. [illegible] will [illegible] the glaze without [illegible] plastic body. [illegible] at a temperature hotter than [illegible]

Note on the Influence of Solvents upon the Formation of Chloracetyldiphenylamine.

By

M. Kuhara and **M. Chikashige.**

Chloracetyl derivatives of aniline and *p*-toluidine were prepared by J. P. Meyer[1] by mixing together chloracetyl chloride and each of the above-mentioned compounds in well-cooled ethereal solutions. Abenius and Widman[2], in applying such process of Meyer to the preparation of the bromacetyl derivative of *o*-toluidine, found it a very unsatisfactory method, since it caused the reaction-products to resinize and made their subsequent purification difficult. It is, however, preferable, as they state, to use benzene, instead of ether, as the solvent in the above case. Furthermore, the chloracetyl derivative of *o*-toluidine was obtained by them in tolerably good yield by using benzene solutions.

Having had particular occasion to prepare a number of the chloracetyl derivatives of different aromatic amines, the authors' attention has naturally been directed to the causes which render the use of ether, as a solvent, disadvantageous. As will be seen by reference to the authors' article[3] on the methyl derivatives of indigo, they find no objection at all to the use of ether, if proper precautions are taken to keep the solutions of chloracetyl chloride and amines sufficiently cold and dilute; and, moreover, the yield is almost always quantitative. When the dilution and cooling of their ethereal solutions are, however, not sufficient,

[1] Ber. d. chem. Gesel. 8, 1158.
[2] J. pr. Chem. [2], 38, 298.
[3] Am. Chem. J., 24, 1.

Abenius and Widman's statement is strictly applicable: the temperature of the reaction is elevated to a considerable extent, and resinization of the products is subsequently caused.

The authors have often attempted to prepare the chloracetyl derivative of diphenylamine by using ethereal solutions of 2 mols. diphenylamine and 1 mol. chloracetyl chloride, according to the method suggested by Meyer as above stated, but the effort always ended in failure. If the reaction in this case be normal, we must accept the following equation:

$$2\ (C_6H_5)_2.NH + Cl.CH_2\,CO.Cl.$$
$$= (C_6H_5)_2.N.OC.CH_2.Cl. + (C_6H_5)_2.NH.HCl.$$

It was, however, quite strange that almost the whole of the product was nothing but the diphenylamine hydrochloride; there being but a trifling yield, or none at all, of chloracetyldiphenylamine. Consequently, we felt constrained to test the process under varying conditions: that is to say, by heating the ethereal solutions of diphenylamine and chloracetyl chloride almost to their boiling points, or by cooling them even to $-15°$, and also to use the materials in their purest possible condition. In every case, the yield of chloracetyldiphenylamine was almost always trifling, and, if the quantities of the materials used in the given case were small, it was almost none at all. Thus we see that even cooling the ethereal solutions of the materials, gives no marked benefit in the production of chloracetyldiphenylamine, but simply results in the change of almost the whole of the diphenylamine used into its hydrochloride.

Admitting that practically almost the total quantity of diphenylamine is transformed into its hydrochloride, the source of the hydrochloric acid should be sought for; because, as will be seen in the equations given above, the liberation of so much hydrochloric acid as to change only half the quantity of diphenylamine used into its hydrochloride is possible. It is highly probable that there may take place a complex reaction before two radicals,

$(C_6H_5)_2N'$ and $CH_2.Cl.CO'$, unite; possibly the ether used as a solvent taking part. Now, assuming the ether to enter the reaction, the following equations may be accounted for:

$$2(C_6H_5)_2.NH + Cl.CH_2.CO.Cl.$$
$$= (C_6H_5)_2.N' + Cl.CH_2.CO' + (C_6H_5)_2.NH.HCl.$$

$$Cl.CH_2.CO' + C_2H_5.O.C_2H_5$$
$$= CH_3.CO.OC_2H_5 + C_2H_3''' + HCl.$$

$$(C_6H_5)_2.N' + C_2H_3''' = (C_6H_5)_2.NH + C_2H_2.$$

$$(C_6H_5)_2.NH + HCl. = (C_6H_5)_2.NH.HCl.$$

Assuming that the reactions take place as in the foregoing equations, the products must be acetic ether and acetylene besides diphenylamine hydrochloride. In fact we detected the presence of acetic ether among the products of the reaction, and also of a gaseous compound which is of an unsaturated nature, owing to its character of decolorizing bromine water, and of forming a heavy oily liquid, yet is not certain of acetylene.

So far, we have been concerned with the matter of fact that chloracetyl chloride and ether do not react on each other at ordinary temperature when mixed; and even when there is present a third substance, such as aniline, toluidines, etc., their mutual action can be prevented by keeping the solutions sufficiently cool and dilute, and the normal reaction can proceed smoothly to the production of the chloracetyl derivatives of those amines. Even in the presence of methylaniline, $CH_3.NH.C_6H_5$, which is similar to diphenylamine in constitution, chloracetyl chloride and ether do not exert mutual action at low temperature, but cause methylaniline to change readily to its chloracetyl derivative.[1]

Now, the reason why the formation of the chloracetyl derivative is hindered in the case of diphenylamine by the presence of ether,

[1] Am. Chem. J., 27, 2.

can be explained by considering the nature of the diphenylamine radical, $(C_6H_5)_2N'$. As is well known, the latter radical is of a highly negative character, owing to the presence of two phenyl groups, and hence possesses less affinity for the radical chloracetyl, $Cl.CH_2.CO'$, than the latter does for ether. Secondary reactions may, therefore, take place as we have described, and they may even go on further, causing the resinization of the products.

Furthermore, the experiments were extended to the action of acetyl chloride upon diphenylamine in the presence of ether, in a similar manner to that in the case of chloracetyl chloride, and these likewise ended in failure, the products simply consisting of diphenylamine hydrochloride and diphenylamine, although Merz and Weith[1] have already obtained acetyldiphenylamine by using benzene as the solvent instead of ether. We further tried to use several indifferent solvents, such as benzene, chloroform, acetone, etc., for the preparation of chloracetyldiphenylamine, and every time found that the reaction proceeded normally, giving almost the theoretical yield.

As a conclusion, we may say that the negative character of the diphenylamine radical is the cause of the secondary reactions which prevent the formation of chloracetyldiphenylamine; and that similar reactions may possibly take place, to some extent, with aniline, toluidines, etc., and chloracetyl chloride in the presence of ether; but in those cases cold and dilution may wholly prevent the progress of the secondary reactions.

The chloracetyldiphenylamine which the authors prepared by using the benzene solutions of diphenylamine and chloracetyl chloride, was analysed and its chlorine determined:

	Found I.	Found II.	Calc. for $(C_6H_5)_2N.CO.CH_2.Cl$.
Chlorine	14.59	14.17	14.46

It is very soluble in ether, benzene, alcohol, etc. It can be separated from its hydrochloride in the benzene solution, by ractional crystallization or by boiling the crude substance with-

[1] Ber. d. chem. Gesel., 15, 11.

water and decanting the melted portion which consists mainly of diphenylamine: it crystallizes in colourless needles, having an irritating odour and acting on the skin. It melts at 112°.

The further investigations are still going on for ascertaining the exact nature of the reaction-products, and the authors expect to communicate the results before long.

明治三十七年三月二十五日印刷
明治三十七年四月二十五日發行

編纂兼發行者　京都帝國大學理工科大學

印刷者　東京市京橋區築地三丁目十五番地
野村宗十郎

印刷所　東京市京橋區築地二丁目十七番地
株式會社東京築地活版製造所

CONTENTS.

Synthesis of Indigo and its Methyl Derivatives. PAGE.
By M. Kuhara and M. Chikashige 1

Ueber die Veränderung der Elektrischen Leitungsfähigkeit eines Pulvers durch Induction.
By H. Muraoka und T. Tamaru 20

On the Filings Coherer and Wireless Telegraphy.
By T. Mizuno 28

Electric Resonance.
By T. Mizuno 33

A Graphical Representation of Potential Drops and Distribution of Currents in a Network System.
By E. Aoyagi 40

Defects of Uncarburetted Water-Gas as Fuel for Laboratory Use.
By M. Chikashige and H. Matsumoto 55

On the Solubility of Gold-Silver Alloys in Potassium Cyanide Solutions.
By J. Yokobori 65

On the Allanite Crystal from Hiei Mountain.
By T. Hiki 72

Deflection and Vibration Diagrams of Kinokawa Railway Bridge Truss.
By S. Tanabe 75

Note on the Body of Awata Pottery.
By H. Matsumoto 77

Note on the Influence of Solvents upon the Formation of Chloracetyldiphenylamine.
By M. Kuhara and M. Chikashige 87

ed. Dec 12 S. 90.
(Box on [illegible])

HARVARD COLLEGE LIBRARY

MEMOIRS

OF THE

COLLEGE OF SCIENCE AND ENGINEERING,

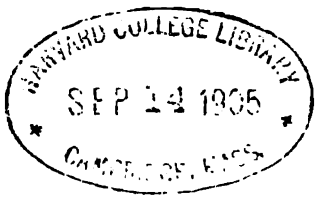
KYŌTO IMPERIAL UNIVERSITY.

VOL. I, No. 2.

KYŌTO.

1904-1905.

Sci 125.40



PUBLICATION COMMITTEE:

Professor	MITSURU KUHARA
Do.	HAN-ICHI MURAOKA
Do.	MASASHI NAMBA
Do.	SAKURŌ TANABE
Do.	TOSHINOJŌ MIZUNO.

These Memoirs contain original articles by the members of the University. They are not intended to be published at regular intervals. Each volume will be separated into 6 numbers of about 100 pages each.

On the Distribution of Iodine between Two Solvents.

By

Yukichi Osaka.

If it should happen that a substance distributes itself between two solvents which do not mix with each other, the ratio of concentration in the two solvents or the coefficient of distribution is constant and independent of the concentration when the substance exists with the same molecular weight in both solutions.[1] Such relation still persists even when a solute is in most part in combination with the solvent, provided that the quantity of the solute in a molecule, either simple or complex, is equal in both solutions and that the solutions are not concentrated. This view will readily be seen from the following considerations:

Let A be a mol of the solute and B that of the solvent, assuming that the solute forms with the solvent a compound which may be represented by AB_m. Then the equilibrium in the solution will be:

$$A + mB \rightleftharpoons AB_m.$$

If we represent the concentrations of those substances by enclosing their formulae in brackets and K be the equilibrium constant of this reversible reaction, then we have the expression:

$$[A] \times [B]^m = K[AB_m]$$

and from this we deduce:

$$\frac{[AB_m]+[A]}{[A]} = 1 + \frac{[B]^m}{K}.$$

Since the solution is dilute: that is; the total amount of A is very small in comparison with that of B, as has been assumed; therefore the formation of the compound, AB_m, has no marked influence on the total amount of the solvent. We may, conse-

[1] See Nernst, Zeitschr. f. physik. Chem. 8, 110, (1891).

quently, take the righthand side of the equation as a constant, and as a result, the concentration of the free part of the solute has a constant ratio to its total concentration in the solution. Now, from what has been stated above, it is obvious that the coefficient of distribution is constant and independent of the concentration, even when the solute combines with the solvent, provided that the solutions are dilute.

The distribution of iodine between two solvents was first investigated by Berthelot and Jungfleisch,[1] using water and carbon bisulphide as solvents, and as a result of their work the coefficient of distribution was found to be constant. Jakowkin[2] studied the same subject with the utmost care, employing the same solvents as a pair, and also water and carbon tetrachloride, as well as water and bromoform, respectively in pairs: he noticed that in all cases the relative amount of iodine in water increases as the concentration of the solution decreases. Concerning this phenomenon he has given an explanation by assuming that iodine in the aqueous solution may exist with a molecular weight corresponding to the formula I_2, while it may be polymerised to I_4 to some extent in other solvents. This assumption, however, does not harmonise with other experimental facts, for the determination of the molecular weight of iodine in solution with different solvents, has always given such a result as to admit the molecular formula I_2,[3] but it is generally accepted, based upon several other observations, that the iodine in the violet-coloured solution exists in a free state, while in the brown-coloured solution it is in combination with its solvent.[4] The formation of

[1] Ann. chim. phys. (4) 26, 396, (1872).

[2] Zeitschr. f. physik. Chem. 18, 585, (1895).

[3] Beckmann, Zeitschr. f. physik. Chem. 5, 78, (1890); Nernst, *ibid.* 6, 16, (1890); Hertz, *ibid.* 6, 358, (1890); Beckmann u. Stock, *ibid.* 17, 107, (1895); etc.

[4] Beckmann, *loc. cit.*; Krüss. u. Thiele, Zeitschr. f. anorg. Chem. 7, 52, (1894); Beckmann u. Stock, *loc. cit.*; Ikeda, Journ. Tokyo Chem. Soc. 19, 120, (1898); Hantzsch u. Vagt, Zeitschr. f. physik. Chem. 38, 705, (1901); Lachmann, Journ. Amer. Chem. Soc. 25, 50, (1903); Strömholm, Zeitschr. f. physik. Chem. 49, 721, (1903); etc.

such a compound as is concerned, in aqueous solution, does not harmonise with Jakowkin's result, since the concentration of the iodine in the aqueous phase was naturally very small, (0·2571 gram of iodine per litre in the most concentrated solution), and consequently any change in the amount of iodine will exert no marked influence on the total amount of the solvent.

The variation in these cases, of the coefficient of distribution with concentration, may likely be due to tolerably high concentration of the iodine in the other solvents, but the nature of the solvents seem to have some considerable influence upon it. The extremes of concentration of the iodine in carbon bisulphide and in bromoform, were 167·6—30·36 and 144·36—22·19 gms. per litre respectively, and the coefficient of distribution showed a variation of about 10 and 20 per cent respectively between these extreme concentrations. In the case of carbon tetrachloride, the coefficient of distribution slightly varied, when the concentration of the iodine decreased from 25·61 to 16·57 gms. per litre, but it remained constant for the variation of the concentration between 16·57 and 4·412.

Regarding the distribution of iodine between chloroform and glycerine, Hantzsch and Vagt[1] observed a considerable variation in the coefficient with concentration. Thus, when the concentration of the iodine in chloroform varied from 0·0216 to 0·00172 mol per litre, the coefficient of distribution showed a variation of about 50 per cent. Now, the assumption, which they have advanced to explain this fact, is that the combination of iodine and solvent may, in some way, take place in the brown solution; but inasmuch as the highest concentration of iodine in glycerine was 0·00782 mol per litre, it is evident that the formation of a compound would exert no remarkable influence on the coefficient of distribution. Strömholm[2] thought that the above mentioned phenomenon could take place only when the glycerine contained some water, for the iodine forms some additional compounds with

[1] *Loc. cit.*
[2] *Loc. cit.*

water, and the latter (present only in an insignificant amount) does not pass over to the chloroform. His explanation, as such, seems not to be satisfactory, however, as will be seen from the following considerations. The additional compounds of iodine with water or glycerine must be in equilibrium with their components, which condition may be represented as follows:

$$I_2(H_2O)_m \rightleftharpoons I_2 + mH_2O$$
$$I_2(C_3H_8O_3)_n \rightleftharpoons I_2 + nC_3H_8O_3$$

Let K_1 and K_2 be the equilibrium constants of the reversible reactions respectively; then we have:

$$K_1[I_2(H_2O)_m] = [I_2] \times [H_2O]^m$$

and

$$K_2[I_2(C_3H_8O_3)_n] = [I_2] \times [C_3H_8O_3]^n$$

and from these we deduce:

$$\frac{[I_2(H_2O)_m] + [I_2(C_3H_8O_3)_n] + [I_2]}{[I_2]} = 1 + \frac{[H_2O]^m}{K_1} + \frac{[C_3H_8O_3]^n}{K_2}$$

or $$\frac{\text{Total concentration of iodine}}{\text{Concentration of free iodine}} = \text{,,} + \quad \text{,,} \quad + \quad \text{,,}$$

Now, since we may assume $[C_3H_8O_3]$ to be constant, $[H_2O]$ is the only variable in the righthand side of the equation, which affects the ratio of the free iodine to the total, and consequently the coefficient of distribution. At any rate, $[H_2O]$ is very small in comparison with $[C_3H_8O_3]$; and, in order that any variation of $[H_2O]$ may have such a remarkable influence on the distribution as Hantzsch and Vagt once observed, K_1 must be enormously small in comparison with K_2. Such relation seems to be quite improbable; yet since we find, up to the present, no suitable explanation to substitute for Strömholm's, the author has lately undertaken the study of the distribution of iodine in another pair of solvents, with a view to contributing some further knowledge on this interesting subject.

According to Tuchschmidt and Follenius,[1] aqueous alcohol, more dilute than 47·90 per cent, is practically inmiscible with carbon bisulphide. The author took these solvents in a pair for his purpose.

The materials were prepared in the following way. Carbon bisulphide was shaken vigorously with metallic mercury and then re-distilled. Commercial absolute alcohol was re-distilled, its concentration estimated from its specific gravity, and it was diluted to the required concentration with so-callen conductivity water. Commercial, resublimed iodine was mixed with about half its weight of potassium iodide, caused to sublime, and then dried over sulphuric acid.

In conducting the experiments, a weighed quantity of iodine was introduced into a well-steamed bottle of about 100 ccm. capacity which was provided with a well-fitting stopper, then 20 ccm. of carbon bisulphide and afterwards 75 ccm. of the aqueous alcohol of known strength were added. The stopper of the bottle was tightly covered with thin caoutchouc cloth, and five similarly-prepared bottles containing different quantities iodine were employed as a set for the purposes of these experiments. The bottles were connected to the stirrer of a thermostat of 25° ± 0·1° C., and the rotation was kept up for a sufficient period of time to ensure equilibrium. 50 ccm. of the alcoholic solution was then taken out of each bottle and the amount of iodine determined by titration with a standard solution of sodium thiosulphate. The concentration of the iodine in carbon bisulphide was not directly determined, but calculated from the amount of same originally taken and that in the alcohol phase. The results of the experiments are given below. In the tables, c and c' denote the amounts of iodine in gms. in 10 ccm. of aqueous alcohol and carbon bisulphide respectively:

[1] Ber. d. chem. Ges. 4, 583, (1871).

$c \times 10^3$	$c' \times 10$	$c/c' \times 10^2$

Table I.

Alcohol: 30·5 gms. in 100 ccm.

0·636	0·490	1·30
1·66	1·322	1·26
2·63	2·050	1·28
3·52	2·690	1·31
5·46	4·227	1·29
		1·29

Table II.

Alcohol: 26·7 gms. in 100 ccm.

0·756	0·980	0·77
1·84	2·376	0·77
3·23	4·284	0·75
3·75	4·899	0·77
4·95	6·510	0·76
		0·76

Table III.

Alcohol: 22·9 gms. in 100 ccm.

1·15	2·378	0·48
1·47	2·987	0·49
2·44	4·892	0·50
3·40	6·892	0·49
4·18	8·961	0·47
		0·49

$c \times 10^3$	$c' \times 10$	$c/c' \times 10^2$

Table IV.

Alcohol: 19·1 gms. in 100 ccm.

0·45	1·342	0·34
0·89	2·484	6·36
1·61	4·546	0·36
2·44	7·040	0·35
3·30	9·700	0·34
		0·34

Table V.

Alcohol: 15·3 gms. in 100 ccm.

0·75	2·561	0·29
1·25	4·458	0·28
1·66	5·826	0·28
2·22	8·408	0·26
3·15	11·534	0·27
		0·28

Table VI.

Alcohol: 11·4 gms. in 100 ccm.

0·77	3·292	0·23
1·48	6·283	0·23
1·83	7·759	0·24
2·44	10·971	0·22
2·80	13·322	0·21
		0·23

$c \times 10^3$	$c' \times 10$	$c/c' \times 10^2$

Table VII.

Alcohol: 7·6 gms. in 100 ccm.

0·72	3·586	0·20
0·95	5·271	0·18
1·33	6·738	0·20
1·67	8·358	0·20
2·11	10·779	0·20
		0·20

As will be seen by reference to the above tables, the author observed some cases in which the relative amount of the iodine in aqueous alcohol shows some tendency to decrease as the concentration of the iodine increases; as had already been noticed by Jakowkin with the pairs of the solutions selected by him: but, on the whole, the variation of the coefficient of distribution is irregular; then it must be taken as constant within the experimental errors.

Those two solvents, aqueous alcohol and carbon bisulphide, are practically inmiscible, yet not absolutely so. If, then, this fact exerts some remarkable influence upon the distribution of the iodine, the variation of the relative amounts of the solvents ought to produce some variation on the coefficient of distribution. In order to determine this point, the author has conducted a series of experiments and has obtained the following results:

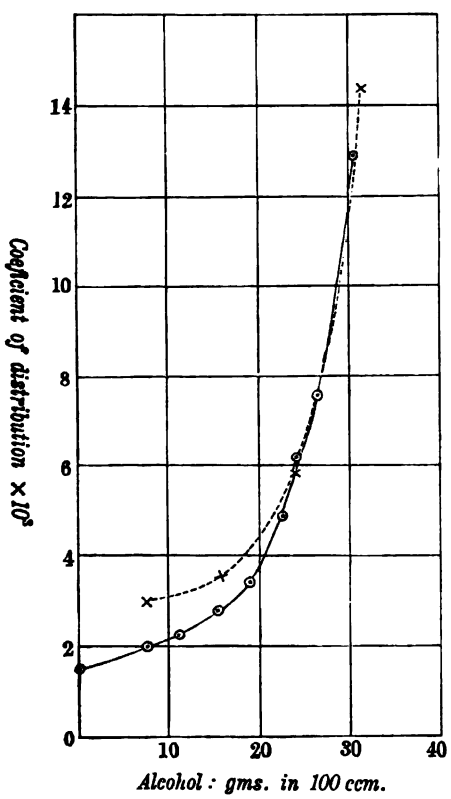
Table VIII.

Relative volumes of the solvents.

Alcohol 24·1 gms. in 100 ccm.	Carbon bisulphide	$c \times 10^3$	$c' \times 10$	$c/c' \times 10^2$
80	15	1·48	2·418	0·61
75	20	1·81	2·957	0·61
70	25	1·80	3·116	0·58
65	30	1·86	3·150	0·59

Alcohol 24·1 gms. in 100 ccm.	Carbon bisulphide	$c \times 10^3$	$c' \times 10$	$c/c' \times 10^2$
60	35	1·88	3·056	0·61
55	40	1·74	2·745	0·63
50	45	1·90	3·016	0·63
45	50	1·96	3·239	0·60
40	55	1·75	2·764	0·63
				0·61

Thus, so far as seen, in the range to which these experiments were extended upon the variation of the relative amounts of the two phases, the coefficient of distribution remains constant within the experimental errors.



As will be seen in the tables given above, the relative concentration of the iodine in aqueous alcohol increases with the concentration of the alcohol; and this relation will be clearly understood by an inspection of the annexed diagram.[1]

Burner[2] measured the solubility of the iodine in carbon bisulphide and in aqueous alcohol of various degrees of dilution. The author has calculated, from Burner's data the ratio of the solubility of iodine in aqueous alcohol and carbon bisulphide, and the relation

[1] In the case of pure water, the author has taken the mean value of Jakowkin.
[2] Zeitschr. f. physik. Chem. 26, 145, (1898).

of the ratios and alcoholic contents are represented in the diagram by a broken line. Burner's figures do not, however, seem to be adapted for such kind of calculation, especially when the alcohol is dilute, as he neglected the solubility of iodine in pure water in comparison with other solvents. According to Jakowkin, the ratio of solubility of iodine in water to that of the same in carbon bisulphide is somewhat less than the coefficient of distribution of iodine between those solvents. It must be remembered that the temperature in Burner's experiments was 14·5°—15·1° C., while that in Jakowkin's, as well as in those of the author, was 25° C., consequently these two sets of cases are not directly comparable. However, the inference established from the above-mentioned relations is that very probably the two curves will approximately coincide, if the observations be made at the same temperature; that is a relation which exists in the case when the two solvents are inmiscible.[1]

[1] Ostwald, Lehrbuch d. allg. Chem. 1, 811, (1903); Jakowkin, *loc. cit.*

On the Equilibrium of the Electrolytic Dissociation of partially neutralised Acids and Bases.

By

Yukichi Osaka.

When a weak monobasic acid is partially neutralised with a strong monoacid base, we have the following equation for the equilibrium of the electrolytic dissociation of the acid which remains free:

$$K(1-\gamma)\frac{a-b}{V}=\left(\frac{b}{V}+\gamma\frac{a-b}{V}\right)\gamma\frac{a-b}{V},$$

where the symbols have the following significance:

K=dissociation constant of the acid.
a =number of mols of the acid.
b = „ „ „ „ „ base.
γ =degree of the electrolytic dissociation of the free acid.
V=volume of the solution.

Here the electrolytic dissociation of the salt is regarded as practically complete and the assumption, as such, is generally admissible when the solution is not concentrated.

Since the acid is weak, γ can be neglected against 1, and if b be not too small in comparison with a, γ $(a-b)$ can also be neglected against b: then the equation will be simplified as follows:

$$K(a-b)=b\gamma\frac{a-b}{V}$$

or

$$C_H=\frac{K(a-b)}{b},$$

where C_H denotes the concentration of the hydrogen ions in the

solution. Thus, the concentration of the hydrogen ions in the solution is constant and independent of dilution.[1]

If we put $a=2b$ in the equation; then we have:

$$C_H=K;$$

that is, when a weak monobasic acid is neutralised by half, the concentration of the hydrogen ions is equal to the dissociation constant of the acid and independent of the dilution of the solution.

Next, we shall take a mixture of two weak monobasic acids and pay attention to the equilibrium when it is partially neutralised with a strong monoacid base. Let a and a' be the number of mols of the two acids and b the number of mols of the base. If x parts of the base neutralise the first acid and $1-x$ parts the second, and if the corresponding terms (as in the case of a single acid) be neglected here again, we have for the electrolytic dissociation of the acids the following equations for equilibrium:

$$K(a-xb)=xbC_H,$$

and

$$K'\{a'-(1-x)b\}=(1-x)bC_H,$$

where K and K' are the dissociation constants of the acids respectively and C_H denotes the total concentration of the hydrogen ions in the solution. Eliminating x between these equations, we have:

$$\frac{aK}{C_H+K}+\frac{a'K'}{C_H+K'}=b.$$

If we take in the equation $a=a'=b$, then we obtain:

$$C_H=\sqrt{KK'};$$

that is, when a mixture of two weak monobasic acids in equivalent proportions is neutralised by half with a strong monoacid base, the total concentration of the hydrogen ions in the solution is independent of dilution and equal to the square root of the product of the dissociation constants of the two acids.

[1] *Cf.* Ostwald, Lehrbuch d. allg. Chem. 11, 2, 194.

Travor[1] measured the velocity of the inversion of cane sugar with the acid salts of dibasic acids as the catalyser, and found that the concentration of the hydrogen ions from the acid salt of a dibasic acid is approximately independent of the dilution of solutions. Noyes[2] studied this relation theoretically and obtained the same expression as has here been derived for a mixture of two monobasic acid in equivalent proportions neutralised by half. It may now easily be shown in the following described manner that an acid salt may be regarded as a particular case of the mixture here dealt with.

In a solution of an acid salt, AHB, we have the ions AH', A'', $H^{\cdot}$ and $B^{\cdot}$, and the electroneutral melecules AH_2, AHB and AB_2. If we denote the concentrations of these ions and molecules by C, subfixing the respective symbols, and the concentrations of the undissociated parts of the salts, AB_2 and AHB, as Noyes assumed, be neglected, then $C_{AH_2}+C_{AH}+C_A$ will represent the total concentration of the acid salt taken and $2C_A+C_{AH}$ that of the cathions in the solution. Since the concentration of the hydrogen ions in the solution is negligible, as we assume, against that of the other cathions, $2C_A+C_{AH}$ may be taken as the concentration of the monoacid base which neutralises the dibasic acid by half; then practically we have:

$$C_{AH_2}+C_{AH}+C_A=2C_A+C_{AH}$$

or

$$C_{AH_2}+C_{AH}=C_{AH}+C_A.$$

Now $C_{AH_2}+C_{AH}$ may be regarded as the total concentration of the acid $(AH)\,H$, both free and neutralised, and $C_{AH}+C_A$ that of the acid AH. Thus a solution of the acid salt of a dibasic acid AH_2 may be considered as equivalent to the mixture of two acids $(AH)\,H$ and AH, in equivalent proportions, which is neutralised by half.

The bases which are partially neutralised may be similarly

[1] Zeitschr. f. physik. Chem. 10, 321, (1892.)
[2] Zeitschr. f. physik. Chem. 11, 495, (1893.)

treated as in the case of acids, and we find for them relations wholly similar to those obtained as above for the latter.

A few years ago, when the author studied the phenomenon of the birotation of d-Glucose,[1] it was found that the velocity constant of the process was approximately proportional to the concentration of the hydroxyl ions in the solution. When, however, the basic hydrochloride of ethylene diamine was used as the catalyser, it was observed that the velocity constant increases considerably with the concentration of the basic salt, while the theory requires that it should be constant. This discrepancy may be partly due to the influence of the salt whose concentration naturally varies with dilution, and which accelerates the catalytic action of the hydroxyl ions; but the variation of the constants with dilution was too great to be duly explained; hence it might be ascribed to some experimental errors not yet noticed. The author has lately undertaken the repetition of experiments in the same way as in the previous case.

For comparison of the water used as the solvent in the present experiments with that used in the previous ones performed in the laboratory of Professor Ostwald in Leipzig, two series of observations were made without any special catalyser being added. The constant was calculated, as usual, by the following formula:

$$k = \frac{1}{t} \log \frac{\alpha_0 - \alpha'_0}{\alpha - \alpha'_0},$$

where α_0 denotes the angle of rotation at the time, arbitrarily taken as the beginning, α'_0 that at the end of the reaction, and α that at any time. The results are as follows:

[1] Zeitschr. f. physik. Chem. 35, 661, (1900.)

t	$\alpha - \alpha_0'$	$\log \frac{\alpha_0 - \alpha_0'}{\alpha - \alpha_0'}$	k
		I.	
0	4·43°	—	—
3	4·12	0·0315	0·0105
6	3·88	0·0576	0·0096
9	3·58	0·0825	0·0092
12	3·30	0·1279	0·0106
16	3·07	0·1583	0·0099
20	2·65	0·2232	0·0112
24	2·27	0·2904	0·0121
30	2·04	0·3368	0.0112
37	1·85	0·3792	0·0102
43	1·52	0·4546	0·0106
51	1·27	0·5326	0·0104
			Mean 0·0105
		II.	
0	4·79°	—	—
3	4·45	0·0319	0·0106
6	4·19	0·0581	0·0097
9	3·82	0·0982	0·0109
12	3·52	0·1338	0·0111
16	3·25	0·1684	0·0106
20	2·97	0·2074	0·0104
25	2·64	0·2587	0·0103
30	2·32	0·3178	0·0106
35	2·12	0·3540	0·0101
42	1·84	0·4155	0·0099
49	1·60	0·4762	0·0097
60	1·24	0·5869	0·0098
			Mean 0·0103

Thus, the constant was found to be 0·0104 as the mean which is concordant with that obtained in the previous experiments.

Then, the experiments were repeated with ethylene diamine neutralised by half with hydrochloric acid as the catalyser. The

results will be given in the following tables, in which v denotes the dilution of the solution; that is, the volume of the solution in litres which contain a mol of the basic salt:

t	$\alpha-\alpha_0'$	$\log\frac{\alpha_0-\alpha_0'}{\alpha-\alpha_0'}$	k
		$v=100.$	
		I.	
0	3·91°	—	—
3	3·53	0·0444	0·0148
5	3·23	0·0830	0·0166
8	2·97	0·1194	0·0149
11	2·73	0·1560	0·0142
14	2·40	0·2120	0·0152
17	2·20	0·2498	0·0147
20	1·89	0·3157	0·0158
23	1·84	0·3274	0·0164
26	1·75	0·3492	0·0152
29	1·54	0·4137	0·0158
32	1·44	0·4348	0·0150
		Mean	0·0159
		$v=100.$	
		II.	
0	4·39°	—	—
3	3·99	0·0415	0·0138
6	3·55	0·0923	0·0154
9	3·14	0·1456	0·0162
12	2·80	0·1953	0·0162
15	2·39	0·2641	0·0176
18	2·22	0·2961	0·0165
21	2·05	0·3307	0·0158
24	1·74	0·4020	0·0167
27	1·50	0·4664	0·0173
30	1·39	0·4995	0·0166
33	1·27	0·5387	0·0163
		Mean	0·0162

t	$\alpha-\alpha_0'$	$\log\frac{\alpha_0-\alpha_0'}{\alpha-\alpha_0'}$	k
		III.	
0	4·28°	—	—
3	3·83	0·0482	0·0161
6	3·37	0·1038	0·0173
9	2·95	0·1616	0·0179
12	2·82	0·1812	0·0150
15	2·48	0·2359	0·0157
18	2·22	0·2850	0·0158
21	2·02	0·3260	0·0155
24	1·70	0·4010	0·0167
27	1·60	0·4273	0·0158
30	1·37	0·4947	0·0164
			Mean 0·0162

$v=200.$

		I.	
0	3·95°	—	—
3	3·47	0·0563	0·0188
6	3·21	0·0901	0·0151
9	2·90	0·1342	0·0149
12	2·68	0·1685	0·0140
16	2·31	0·2330	0·0146
20	1·95	0·3066	0·0154
24	1·76	0·3511	0·0146
28	1·66	0·3765	0·0134
32	1·46	0·4322	0·0134
36	1·35	0·4663	0·0130
			Mean 0·0147

t	$\alpha-\alpha_0'$	$\log \frac{\alpha_0-\alpha_0'}{\alpha-\alpha_0'}$	k
		II.	
0	4·12°	—	—
3	3·75	0·0409	0·0136
6	3·30	0·0964	0·0161
9	3·05	0·1306	0·0145
12	2·81	0·1662	0·0138
15	2·57	0·2052	0·0137
18	2·22	0·2685	0·0149
21	2·03	0·2968	0·0142
24	1·83	0·3524	0·0148
27	1·65	0·3974	0·0147
30	1·50	0·4388	0·0146
			Mean 0·0146
		III.	
0	4·34°	—	—
3	3·90	0·0464	0·0155
6	3·57	0·0848	0·0141
9	3·27	0·1230	0·0137
12	2·79	0·1919	0·0160
15	2·64	0·2159	0·0144
18	2·24	0·2873	0·0159
21	2·14	0·3071	0·0146
24	2·00	0·3365	0·0140
27	1·69	0·4096	0·0152
30	1·49	0·4643	0·0154
33	1·39	0·4945	0·0150
			Mean 0·0149

t	$\alpha-\alpha_0'$	$\log\frac{\alpha_0-\alpha_0'}{\alpha-\alpha_0'}$	k
		$v=400$.	
		I.	
0	4·60°	—	—
3	4·17	0·0427	0·0142
6	3·85	0·0773	0·0129
9	3·58	0·1089	0·0121
12	3·28	0·1469	0·0122
15	2·95	0·1930	0·0129
18	2·77	0·2203	0·0124
21	2·57	0·2529	0·0120
24	2·37	0·2881	0·0120
27	2·17	0·3263	0·0121
30	2·07	0·3468	0·0116
34	1·75	0·4198	0·0125
			Mean 0·0124
		II.	
0	4·47°	—	—
3	4·07	0·0407	0·0136
6	3·70	0·0821	0·0137
9	3·28	0·1344	0·0149
12	3·17	0·1492	0·0124
15	2·92	0·1849	0·0123
18	2·67	0·2238	0·0124
21	2·40	0·2701	0·0129
24	2·27	0·2943	0·0122
27	2·03	0·3428	0·0127
30	1·92	0·3770	0·0126
34	1·65	0·4328	0·0127
			Mean 0·0129

t	$\alpha - x_0'$	$\log \frac{x_0 - x_0'}{\alpha - x_0'}$	k
		III.	
0	5·33°	—	—
3	4·95	0·0339	0·0113
6	4·42	0·0813	0·0136
9	4·13	0·1107	0·0123
12	3·75	0·1527	0·0127
15	3·52	0·1802	0·0120
18	3·20	0·2216	0·0124
21	2·97	0·2539	0·0120
24	2·45	0·3375	0·0141
27	2·37	0·3520	0·0130
30	2·27	0·3707	0·0124
33	2·13	0·3983	0·0120
36	2·02	0·4213	0·0118
			Mean 0·0125

The mean value of the constant for each of the three dilutions is as follows:

v	k
400	0·0126
200	0·0147
100	0·0161

As will be seen, the constant varies with dilution; but the variation is much smaller than that in the previous experiments, and, moreover, the values obtained in the present experiments are remarkably smaller.

In the experiments with the mixtures of ammonia and ammonium chloride as the catalyser, the velocity constants were approximately proportional to the concentration of the hydroxyl ions, as theoretically calculated from the known composition of the solution, but the constant was too great when the con-

centration of the neutral salt was comparatively high. The latter fact, as above remarked, may explain the comparatively small variation of the constant observed. In the cases with ammonia and ammonium chloride, the following approximate relation has been found:

$$\frac{k}{C_{OH}} = 1{\cdot}3 \times 10^4,$$

If we calculate by this expression the concentrations of the hydroxyl ions in the solutions investigated, we have approximately:

v	$C_H \times 10^6$
400	1
200	1·1
100	1·2

According to Bredig[1], the dissociation constant of ethylene diamine with respect to the first hydroxyl is:

$$K = 0{\cdot}000085$$

and from the formula, $C_{OH} = \sqrt{KK'}$, it follows for the constant K' of the second hydroxyl:

$$K' = 1{\cdot}4 \times 10^{-8}.$$

This value is evidently merely an approximate one, but nevertheless the dissociation constant of ethylene diamine with respect to the second hydroxyl will be of this order.

[1] Zeitschr. f. physik. Chem. 13, 308, (1894.)

Action of Ammonia and of Amines upon Chloral.

By

Mitsuru Kuhara and **Yoshinori Kishi.**

In his article on the constitution of chloralammonia and aldehydammonia, Schiff[1] states that in the preparation of chloralammonia by Personne,[2] ammonia acts upon chloral in two different ways at the same time, viz. partly to form the addition product, chloralammonia, and partly to produce cholroform and formamide, as is represented by the following equations:

1. $CCl_3 \cdot COH + NH_3 = CCl_3 \cdot CH \cdot NH_2 \cdot OH$,
2. $CCl_3 \cdot COH + NH_3 \quad CCl_3H + H \cdot CO \cdot NH_2$.

He further states that, in order to keep the chloral from such destructive action of ammonia which is not directly added, it is necessary to use a liquid in which ammonia is only slightly, or not at all, soluble as a solvent for chloral. He used chloroform for this purpose, and succeeded in getting tolerably good results by conducting the process with the chloroform solution (1 vol. chloral and 1½ vols. chloroform), cooled with ice and salt, into which a rapid current of ammonia was passed until the entire contents of a vessel solidified into a compact mass. The moment solidification takes place, he states, the passing of ammonia must be discontinued, otherwise it exerts a destructive action upon the chloralammonia already formed, since the chloral will have been completely exhausted.

The present authors can hardly concur with the view that the action of ammonia upon chloral takes place in two different ways at the same time; but there are some grounds for admit-

1 Ber. d. chem. Ges. **10**, 167.

2 Ann. d. Chem. **157**, 113.

ting that the reactions are successive: that is to say, chloral-ammonia is first produced by the addition of ammonia upon chloral, and subsequently decomposes, either by the further action of the ammonia or by itself by the heat generated in the reaction.

The process employed by Schiff[1] for the preparation of chloralammonia was repeated by the authors with the following described arrangement, for the purpose of avoiding the elevation of temperature by all possible precautions. Into a solution of chloral dissolved in six times its volume of chloroform and cooled to $-16°$ with ice and salt, a current of ammonia gas, likewise cooled to $-16°$ by passing it through a spiral tube surrounded with same freezing mixture, was admitted. This was continued for four hours, no rise in temperature being noticed during the experiment. No crystals of chloralammonia were deposited, as the solution was dilute. On quickly evaporating the solution, by blowing off the chloroform with a bellows, the chloralammonia was deposited as crystals, which were dried and weighed. The yield was very near to the theoretical.

Other experiments, based upon the assumption that the decomposition by ammonia of chloralammonia in the chloroform solution may possibly take place by some elevatian of temperature, were then undertaken. 5 grams of chloralammonia were dissolved in 25 grams of chloroform, and into the solution, kept constantly at 0°, was passed dry ammonia gas, likewise cooled to 0° with the same arrangement as in the preceding experiment. After two hours the solution was quickly evaporated to dryness in the same manner as already described, and the crystalline residue, which had been dried under a desiccator, was weighed; but almost no change from the original weight was observed. By repeating the same experiment, but at other and different temperatures, viz. at 8°, 14°, 30° and 40°, again almost no alteration was noticed in the weight of chloralammonia originally taken in each experiment.

[1] Loc. cit.

According to the results of the foregoing experiments, it seems as if ammonia can hardly exert its decomposing action upon chloralammonia in the chloroform solution. But it readily acts upon solid chloralammonia, even at a low temperature, decomposing it chiefly into chloroform and formamide. The authors carried on the experiment by gently passing dry ammonia gas, having a temperature of 14°, into 5 grams of finely powdered chloralammonia, also kept almost constantly at 14°. The chloralammonia soon began to liquify, owing to its decomposition into chloroform and formamide, which slowly progressed, and, on continuing the passing of the gas for about two hours, completely decomposed. By repeating the experiment at 0° and at −10°, exactly the same results were obtained. Moreover, it was noticed that when the current of ammonia gas is very slowly passed, apparently no decomposition takes place; but that when the passage of the gas is very rapid, the decomposition immediately begins and proceeds with considerable rapidity. Hence it is evident that the interaction of ammonia and chloralammonia is greatly influenced by mass.

The authors were then led to doubt if the solubility of ammonia in chloroform exerts an influence upon the decomposition of chloralammonia dissolved in the same solvent, and its solubility was then ascertained with approximate accuracy at 14° under 758 mm., the results of the experiments being given below:

C. c. solution.	Gram ammonia.	% Ammonia.	Mols. amm. per liter.
10	0·4379	2·76	2·57
10	0·4457	2·81	2·62
10	0·4252	2·68	2·50
10	0·4462	2·81	2·62
	Mean 0·4388	2·76	2·57

Since ammonia is somewhat soluble in chloroform, as will be seen from the above table, certain experiments were undertaken to determine what influence ammonia, contained in its saturated chloroform solution, will exert upon chloralammonia dissolved in

one and the same solution. For this purpose, different quantities of chloralammonia, dissolved in a definite quantity of the saturated chloroform solution of ammonia, were allowed to stand for certain periods of time at 4° — 14°, after which each solution was evaporated to dryness in vacum, and the phenomena of the decomposition were noted, as will be seen below:

	C. c. sat. chloroform solution of ammonia taken.	Gram chloralamm. dissolved.	Ammonia corres. normal.	Chloralamm. corres. normal.	Hours stood.
I	36·6	1·5	2·5	0·25	116
II	36·6	3	2·5	0·5	195
III	36·6	6	2·5	1	265
IV	36·6	9	2·5	1·5	265

In experiments I and II, the chloralammonia was found to have been decomposed almost entirely; while in III and IV, partial decomposition was effected, probably requiring a great expenditure of time to reach the end of reaction on account of the higher concentration. However, by passing a rapid current of ammonia gas for nine hours into 36·6 c.c. of the saturated chloroform solution of ammonia, in which 1·5 gram of chloralammonia were dissolved, (corresponding to 2½ normal ammonia and ¼ normal chloralammonia), the greater part of the latter was observed to have been decomposed. On keeping for twenty-four hours the same solution of chloralammonia charged with ammonia under the increased pressure by its rapid passage, the decomposition was found to have been completeiy effected. It is evident, from these experiments, that in fact the decomposition of chloralammonia in the chloroform solution will be effected by ammonia and be considerably facilitated by increasing the concentration of the ammonia.

With regard to the advantage of using chloroform in the preparation of chloralammonia as a solvent, the authors submit their explanation on the assumption that the additive action of ammonia upon chloral progresses rapidly so long as free chloral is present in the solution; but when the latter has been exhausted

by the formation of chloralammonia, ammonia will interact exceedingly slowly with chloralammonia in the chloroform solution, as the amount of ammonia which dissolves in the same solvent under ordinary conditions will not be sufficient for the rapid interaction if the chloralammonia present in the solution is relatively large in amount.

It is well known that chloralammonia melts at 62°—64°, above which the higher the temperature rises, the more it decomposes; but its complete decomposition, chiefly into chloroform and formamide, takes place at 100° and is accompanied by certain secondary reactions. The authors tried to pass ammonia gas, cooled to —16°, direct into free chloral, (of which 7 grams were used,) also cooled to —16°, being kept in a freezing mixture, without using any solvent. The temperature gradually rose during this experiment to 65°, (the melting point of chloralammonia), owing to the formation of chloralammonia, but, on slightly cooling the latter soon solidified into a hard mass. On conducting ammonia gas to chloral at the ordinary temperature, however, intense evolution of heat was caused, which raised the temperature to 103°; producing no chloralammonia at all, but simply giving chloroform, formamide, and some ammonium chloride. Hence, it is obvious, from the last case, that chloralammonia formed by the addition of ammonia upon chloral immediately decomposes, on being exposed to a temperature above 100° by the heat evolved in the reaction.

It is, therefore, highly probable that in Personne's[1] experiment, the formation of chloroform and formamide was due either to the destructive action of ammonia upon chloralammonia produced in solid form, as no solvent was used, or to the decomposition of chloralammonia by itself, owing to the rise of temperature by the heat generated in the reaction, which might have occurred from insufficient cooling.

From what has been described of the foregoing experiments,

[1] Loc. cit.

the reactions of the decomposition of chloral by ammonia, may be distinguished as the following two kinds:

(1) At ordinary temperatnre, ammonia acts upon chloral so as to form the addition product, chloralammonia, which will immediately decompose of itself into chloroform and formamide chiefly, owing to the remarkable elevation of temperature by the heat evolved in the reaction. The mechanism of this reaction may be represented thus:

$$1.\quad CCl_3{\cdot}COH + NH_3 = CCl_3{\cdot}CH{<}^{NH_2}_{OH},$$

$$2.\quad \begin{matrix} CCl_3 \\ H \end{matrix}\!\!\begin{matrix} \vert \\ \vert \end{matrix}\!\!\begin{matrix} \\ O \end{matrix}{>}C{<}^{NH_2}_{H} = CCl_3H + O{=}C{<}^{NH_2}_{H}.$$

(2) At low temperature, ammonia likewise acts upon chloral so as to form chloralammonia, which will remain undecomposed if its action be timely discontinued; but if the action of the ammonia be continued further, the chloralammonia will be decomposed into chloroform and formamide. The mechanism of the reactions may be represented as follows:

$$1.\quad CCl_3{\cdot}COH + NH_3 = CCl_3{\cdot}CH{<}^{NH_2}_{OH},$$

$$2.\quad \begin{matrix} CCl_3 \\ H \end{matrix}\!\!\begin{matrix} \vert \\ \vert \end{matrix}\!\!\begin{matrix} CH{<}^{NH_2}_{OH} \\ NH_2 \end{matrix} = CCl_3H + CH{<}^{NH_2}_{\substack{OH \\ NH_2}},$$

$$3.\quad CH{<}^{NH_2}_{\boxed{O\boxed{H}}}{\boxed{NH_2}} = NH_3 + CH{<}^{NH_2}_{O}.$$

Next, the authors ascribe the formation of the formyl derivatives of amines, especially aliphatic, by chloral, to the analogy with the decomposition of chloral by ammonia. Hofmann[1] noticed the production of ethylenediformyldiamide, $C_2H_4(NH{\cdot}COH)_2$, by mixing ethylenediamine and chloral together, which act energetically upon each other with separation of chloroform. The

[1] Ber. d. chem. Ges., 5, 247.

authors repeated the experiment, using the two substances cooled to 0°: when mixed in molecular proportions, the temperature was suddenly raised to 75°; again, they tried the same at ordinary temperature, when the reaction was more energetic, attended by a rise of temperature to 98°, chloroform and ethylenediformyldiamide resulting in each experiment. It is, therefore, assumed that there is first formed the addition product of ethylenediamine with chloral, which immediately decomposes by the heat generated in the reaction, as will be seen:

$$1.\quad \begin{matrix} CCl_3{\cdot}COH \\ CCl_3{\cdot}COH \end{matrix} + \begin{matrix} H_2N{-}CH_2 \\ | \\ H_2N{-}CH_2 \end{matrix} = \begin{matrix} CCl_3{-}CH{<}\begin{matrix} OH \\ NH{-}CH_2 \end{matrix} \\ | \\ CCl_3{-}CH{<}\begin{matrix} NH{-}CH_2 \\ OH, \end{matrix} \end{matrix}$$

$$2.\quad \begin{matrix} H \\ CCl_3 \\ CCl_3 \\ H \end{matrix}\Big|\begin{matrix} O \\ \\ \\ O \end{matrix}\!\!>\!CH{-}NH{-}CH_2 \;\; \begin{matrix} \\ | \\ \\ \end{matrix} = \begin{matrix} O{=}CH{-}NH{-}CH_2 \\ | \\ O{=}CH{-}NH{-}CH_2 \end{matrix} + CCl_3H.$$

Hofmann[1] also obtained ethylformamide by heating the product formed from the direct union of ethylamine and chloral. This shows that the addition product is evidently chloralethylamine and decomposes of itself under the influence of heat; the reaction being:

$$1.\quad CCl_3{\cdot}COH + NH_2{\cdot}C_2H_5 = CCl_3{\cdot}CH{<}\begin{matrix} NH{\cdot}C_2H_5 \\ OH, \end{matrix}$$

$$2.\quad \begin{matrix} CCl_2 \\ H \end{matrix}\Big|\begin{matrix} \\ O \end{matrix}\!\!>\!C{<}\begin{matrix} NH{\cdot}C_2H_5 \\ H \end{matrix} = CCl_3H + O{=}C{<}\begin{matrix} NH{\cdot}C_2H_5 \\ H. \end{matrix}$$

When, however, aromatic amines such as aniline or toluidines act upon chloral, the reaction proceeds in an entirely different manner: that is, diphenyl or ditolyl derivatives of trichlorethylidenediamine—$CCl_3{\cdot}CH(NH{\cdot}C_6H_5)_2$ or $CCl_3{\cdot}CH(NH{\cdot}C_6H_4{\cdot}CH_3)_2$[2]—are produced instead of their formyl derivatives. Such characteristic difference as is recognized in the aromatic amines, depends upon the weakness of their basic property. The relative strengths of the basic property of ammonia and amines, will be seen from

[1] Ber. d. chem. Ges., 5, 251.

[2] Ibid.

the well known dissociation constants (K) of the bases they form; as is shown in the following table for reference:

Ammonia	$NH_4 \cdot OH$	$2 \cdot 3 \times 10^{-5}$
Methylamine	$CH_3 \cdot NH_3 \cdot OH$	$5 \cdot \times 100^{-5}$
Ethylamine	$C_2H_5 \cdot NH_3 \cdot OH$	$5 \cdot 3 \times 10^{-5}$
Ethylenediamine	$C_2H_4(NH_3 \cdot OH)_2$	$8 \cdot 5 \times 10^{-5}$
Benzylamine	$C_6H_5 \cdot CH_2 \cdot NH_3 \cdot OH$	$2 \cdot 4 \times 10^{-5}$
Aniline	$C_6H_5 \cdot NH_3 \cdot OH$	$5 \cdot 3 \times 10^{-10}$
p-Toluidine	$C_6H_4 \cdot CH_3 \cdot NH_3 \cdot OH$	$1 \cdot 9 \times 10^{-9}$

Even of the aromatic amines, benzylamine, which possesses almost the same value of dissociation constant as ammonia—as is shown in the foregoing table,—reacts with chloral as energetically as ammonia does, producing chloroform and benzylformamide. From this, it is obvious that the decomposition of chloral by amines, depends upon the strength of their basic property.

Benzylformamide, $C_6H_5 \cdot CH_2 \cdot NH \cdot COH$.—2 mols. benzylamine and 1 mol. chloral being mixed together, produced a syrupy liquid with evolution of heat. After heating the mixture still further over a water bath, in a flask provided with an ascending tube, the chloroform produced was distilled off and the residual thick liquid dissolved in ether. On passing hydrochloric acid gas into the ethereal solution, the benzylamine left unchanged was precipitated as the hydrochloride and was removed by filtration. The residual semi-solid, left on evaporating the filtrate, solidified all in a moment, but after a certain time had elapsed, and the solid obtained was dissolved in alcohol. From this solution the crystals were deposited on evaporation, when they were washed with petroleum ether and then recrystallised from alcohol. The crystals had all the properties of benzylformamide, melting at 48°–50°, as described by Hollemann.[1]

As has been already stated, the ordinary aromatic amines, such as aniline or toluidines, can not decompose chloral, or, in other words, do not produce their formyl derivatives by chloral.

[1] Rec. trav. chim., **13**, 414.

They form their formyl derivatives, however, very readily with chloralammonia instead of free chloral. But it has been found that their formation depends solely upon the secondary reaction, and not the direct one between the aromatic amines and chloralammonia. On heating a mixture of an aromatic amine and chloralammonia together, the latter itself first decomposes into formamide and chloroform, and the formamide so formed reacts upon the amine, producing its formyl derivative, like the formation of formylpiperidine,[1] as may be represented by the general equation:

$$ArNH_2 + NH_2{\cdot}COH = ArNH{\cdot}COH + NH_3.$$

Such formation of formyl derivatives from ordinary aromatic amines and chloralammonia, will be shown to be applicable as a general method, by the experiments which will be described hereinafter.

Formanilide,[2] $C_6H_5{\cdot}NH{\cdot}COH$.—A mixture of the molecular proportions of chloralammonia and aniline, on being heated over a water bath, became reddish brown, violently evolving ammonia, and at the same time precipitating some ammonium chloride: the odor of isonitril and of chloroform being also recognized. After continuing the heating for a while, the chloroform was distilled off from the mixture, and the residual liquid dissolved in ether to separate ammonium chloride. The ethereal solution was evaporated, and after the oily residue had been treated with dilute hydrochloric acid, to remove unchanged aniline, it was washed with water, dried, and dissolved in alcohol. The alcoholic solution was then mixed with the alcoholic solution of sodium hydroxide, whereupon sodium formanilide,[3] $C_6H_5{\cdot}NNa{\cdot}COH$, was precipitated in a crystalline state. This was first washed with a little alcohol and finally wlth alcohol-ether, dried under a desiccator, and analysed. The following results show it to be sodium formanilide:

1 Monatsh., **9**, 700.

2 Ann. d. Chem., **142**, 121; Ber. d. chem. Ges., **15**, 2443.

3 Ber. d. chem. Gesel., **15**, 2480.

	Calculated for $C_6H_5 \cdot NNa \cdot COH + H_2O$.	Found. I.	Found. II.
Sodium.	14·51	14·20	14·13

In order to confirm the formation of formanilide from formamide and aniline, the molecular proportions of aniline and specially prepared pure formamide were heated over a water bath, by which process an energetic evolution of ammonia took place, and a syrupy substance was produced. The latter was treated with hydrochloric acid, washed with water, dried under a desiccator, and afterwards dissolved in alcohol. The sodium formanilide, which was precipitated from this alcoholic solution and treated in the same manner as the preceding, was dried under a desiccator for over two weeks, and then analysed; the result being as follows:

	Calculated for $C_6H_5 \cdot NNa \cdot COH$.	Found.
Sodium.	16·11	16·47

Form-o-toluide, $C_6H_4 \cdot CH_3 \cdot NH \cdot COH$.—A mixture of chloral-ammonia and o-toluidine was treated in the same way as the formanilide, and finally the thick liquid substance produced was distilled under diminished pressure. The distillate solidified on standing a while. The solid substance obtained was washed with hydrochloric acid and crystallized out from the alcoholic solution in plates. It melted at 62°, as Nef[1] states, and has all the other properties of form-o-toluide described by Ladenburg.[2]

Form-p-toluide, $C_6H_4 \cdot CH_3 \cdot NH \cdot COH$.—After heating molecular proportions of chloralammonia and p-toluidine together over a water bath, as in the preceding experiments, the resulting substance was dissolved in alcohol. To this solution, alcoholic solution of sodium hydroxide was added, but no precipitate was produced. On adding ether to the solution, however, sodium form-p-toluide[3] separated out in the form of scaly crystals with a pearly lustre. The precipitate, when analyzed, gave the amount of sodium as follows:

[1] Ann. d. Chem., **270**, 310.
[2] Ber. d. chem. Ges., **10**. 1129.
[3] Ibid., **13**, 2451.

	Calculated for $C_6H_4{\cdot}CH_3{\cdot}NNa{\cdot}COH$.	Found. I.	II.
Sodium	14·67	14·75	14·58

Form-α-m-xylide[1], $C_6H_3{\cdot}CH_3{\cdot}CH_3{\cdot}NH{\cdot}COH$. — On heating a mixture of α-m-Xylidine and chloroform as before, reaction took place with separation of ammonium chloride; the odor of isonitril being evolved. The reaction product, after standing for a while, deposited the crystals. These were washed with ether, dilute hydrochloric acid, and water successively, and finally dissolved in boiling water; from which solution colourless, fine, needle-shaped crystals separated out on cooling. This substance, purified by repeated recrystallisation, melted at 112°–114°, which is known to be the melting point of form-α-m-xylide.

Form-pseudocumidide[2], $C_6H_3{\cdot}CH_3{\cdot}C_3H_7{\cdot}NH{\cdot}COH$.—The formation of this compound from pseudocumidine and chloralammonia, followed the same process as form-α-m-xylide. The resulting substance was purified by repeated recrystallization from boiling water. The crystals were colourless needles, and melted at 121°–123°.

Form-α-naphthalide[3], $C_{10}H_7{\cdot}NH{\cdot}COH$.—The process of the formation of this compound from α-naphthylamine and chloralammonia is the same as in the case of form-pseudocumidide. The substance crystallized out from the aqueous solution in the form of pink-coloured, silky needles. It melted at 138°–139°.

Form-β-naphthalide[4], $C_{10}H_7{\cdot}NH{\cdot}COH$.—The process for its production from β-naphthylamine and chloralammonia is the same as for the α-variety. It crystallized from boiling-water in the form of plates slightly rose-coloured. Its melting point was 128°.

[1] Ber. d. chem. Ges., **18**, 1011.
[2] Ibid., **18**, 2296.
[3] Ann. d. Chem., **108**, 229; Ber. d. chem. Ges., **15**, 2447.
[4] Ann. d. Chem., **11**, 58; Ibid., **211**, 421; Ber. d. chem. Ges., **15**, 2447.

December, 1904.

Occurrence of Cerasite and Chiastolite in a Metamorphosed Clay Slate.

By

Tadasu Hiki.

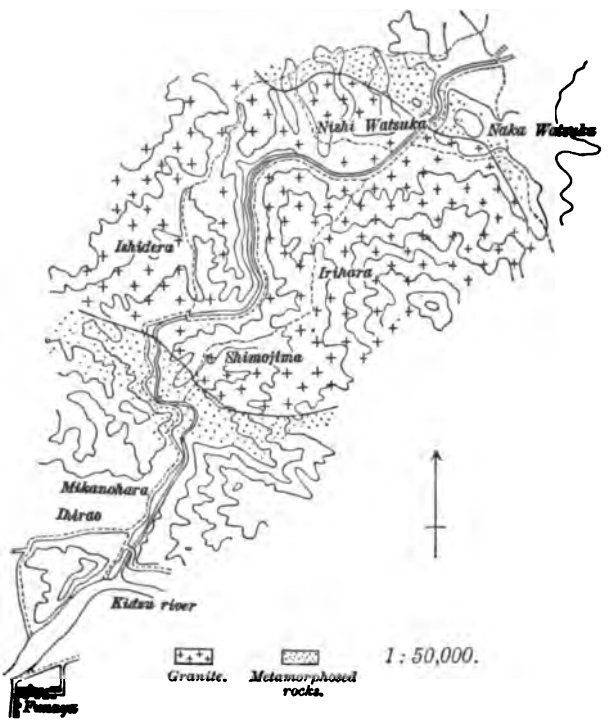
The occurrence of cerasite and chiastolite in clay slate at the *aureola* of the granite bosses, due to the influence of contact metamorphism, is a subject fully discussed by the late Y. Kikuchi.[1] At the time of his investigations, however, the localities of both minerals were very limited, hence he was unable to make full comparison with many instances. The places in which he specially studied of cerasite, were the Watarasegawa region of Shimotsuke province, and the Kameoka district of Tamba province. After minute examination, he found cerasite to be a variety of cordierite characterized by the constant and regular form of the enclosing foreign materials, and by the absence or weakness of pleochroism. A brief note concerning chiastolite, as found in the crystals from the Usuginu region of Rikuchu province and from Mount Tsukuba in Hidachi province, has also been left by the same writer.[2] Recently, many localities for both minerals have been discovered, where the granite pierces through the paleozoic formation.

It is well known that, whenever granite has protruded through paleozoic rocks, such as hornstone, greywackesandstone, clay slate, limestone, etc., contact metamorphism results along the margin of those rocks. Thus, sandstone is altered into a fine,

[1] Journ. Sc. Coll. Univ., Tokyo, Vol. III. part 4.
[2] Journ. Geographical Society, Tokyo, Vol. II.

granular, light violet-grey quartzite, characterized by the development of biotite; the hornstone is converted into micaceous quartzite; the clay slate is either transformed into micaceous slate, or develops new mineral without remarkable sign of metamorphism; and the limestone changes into fine-grained marble, associated with various lime-silicates. The new mineral developed is either cerasite or chiastolite. So far as the author has observed, the most frequently occurring mineral, in many instances, is cerasite; although the chiastolite is seldom found under the same conditions and in the same rock, but in different localities. Although each has certain characteristics peculiar to itself, there must be a

Fig. I.



close general relation between two; but, unfortunately, the author has been unable until recently to get the best specimens with which to determine that relation.

The brief account, which is now to be given, is the description of the places where the minerals occur together in a quite narrow space at the margin of the granite; perhaps it may give an idea of the formation of the minerals.

In the southern part of Yamashiro province, there is a small village of Funaya (called, also, Kamo) on the southern bank of the river Kidzu: it is six kilometres distant from Nara, a famous old town. Near the northern bank of the river, a large granite mass extends from east to west, outcropping through the paleozoic formation over extensive area. It becomes very narrow near Funaya, crossed by the Idzumigawa, a small tributary of the Kizugawa. At the ends of the granite outcrop we find two villages, Mikanohara on the south and Watsuka on the north, as shown in Fig. 1. These two villages are about four kilometres distant to each other. In both places, the granite is crossed by many small dikes, owing to the presence of which the neighbouring paleozoic rock is found to have effected the metamorphic changes. Now, it is proposed to discuss the geological conditions in both places separately.

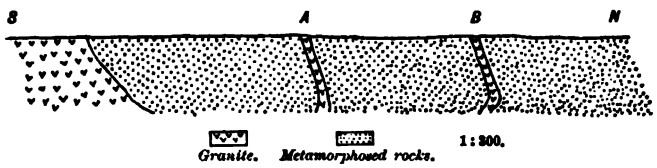
Watsuka Region.

At the boundary of the villages, Naka-Watsuka and Nishi-Watsuka, is a hill on the northern end of the granite mass, and the upper course of the Idzumigawa (called locally Watsukagawa) cuts through the hill and flow from north to south. In the bank of the stream, there is found a series of fresh exposures of metamorphic rocks, water-worn, so clearly defined that we can readily observe the changes in the rock. The exposures in the bank extend for about two hundred metres from the granite exposure towards the upper course. There are two granite dikes, A and

B (Fig. II.), at the distances of eighty-two and one hundred fifty-four metres respectively, from the main body of the granite.

Fig. II.

Section along the river.



The author could not observe the continuous relation of all the complex on account of the discontinuity of the strata. The complex is the series of clay slate and greywackesandstone, bearing N. 60° W., and dipping 70° to the south; and this is the general direction of the rock all over the vicinity. The zones, at the periphery of the dikes, containing the new minerals, are very narrow, and are of the following dimensions:

Dike A	northern side . .	30 centimetres.
	southern side . .	5 metres.
Dike B	northern side . .	4 metres.
	southern side . .	3·25 metres.

Apparenty, the various steps in the change are not always the same, but the different characteristics being indicatcd by the stratigraphical order given in Figs. III. and IV.

Now the details of the rocks will be explained.

Biotite Granite.

The main granite, which gives the contact phenomena to the paleozoic rocks, is the normal biotite granite. It is a light-coloured, coarse granular, holocrystalline variety, consisting of orthoclase, quartz, somé plagioclase and biotite occurring tògether. The felspars are comparatively fresh, but the orthoclase has undergone some

Fig. III.

Section along the river through the granite dike B.

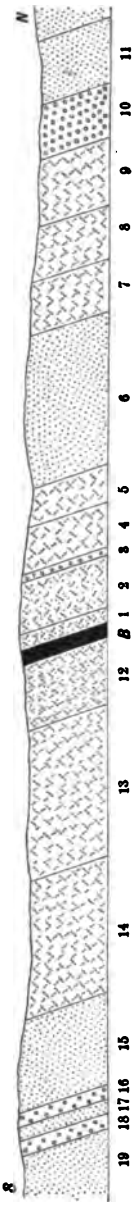
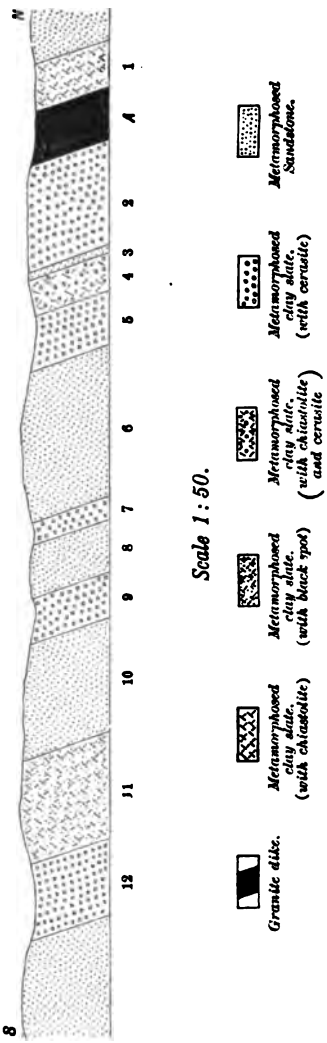


Fig. IV.

Section along the river through the granite dike A.



decomposition. The quartz is variously fissured and cracked, forming the greater part of the rock. The fresh, idiomorphic biotite of deep brown colour and intense pleochroism is common. A peculiarity of this rock is the association of pink-coloured garnet at the periphery of the mass which is of the same character as the following mentioned dike rocks.

Granite Dikes.

(Dike A.....thickness 35 cm.; Dike B.....10 cm.)

These granite dikes interpenetrate the paleozoic rock complex from the main mass. They are made up of moderately fine granular quartz and felspar, in nearly equal proportions. White mica flakes predominate and frequently develop into large plates. A few crystals of pink-coloured garnet (about one millimetre in diameter) are distributed through the mass: they remain comparatively fresh *in situ*, on account of the river erosion.

Spctted Clay Slate.

It is a greyish-black, compact, more or less fissile clay slate, and the trace of metamorphism can scarcely be observed in it. Well-marked black spots (cross section, 1–2 mm.; 5–6 in number, in 1 c.c.) are irregularly developed through this rock. Under the microscope the general ground mass is shown to consist of a large quantity of carbonaceous matter, with newly developed, pleochroic, brown biotite flakes, as that in many other localities. The spots occur in two different forms; one of them consists of a clear, transparent mineral, enclosed by the aggregation of biotite flakes which are little larger than those of the ground mass. Under crossed nicols, it appears to be the aggregation of the granular mineral showing vivid polarization colour, like the aggregation of muscovite. Judging from the character, the mineral may be identified as the chiastolite of the imperfect state of growth.

Another variety of these spots consists of an indeterminable, formless mineral, without distinct demarcation from the ground mass. It is an aggregation of varying quantities of biotite and carbon particles, intermixed with transparent grains; it is probably chiastolite which does not present such vivid colouring as that hereinbefore mentioned. These two different spots may be considered to consist of the same mineral. The zones which define this rock are as follows:

Dike B, 1. . . . 10 cm. in thickness.
„ B, 7. . . . 35 cm. „ „

In the last zone, besides the above-mentioned facts, narrow bands of strata, containing small quantities of cerasite in an imperfect condition, intercalate in the lenticular forms.

Dike B, 8. . . . 35 cm. in thickness.

Spotted Chiastolite Clay Slate.

It is a compact greyish-black clay slate, resembling spotted clay slate. The characteristic feature is the development of numerous sharply defined rhombic crystals of chiastolite of a white colour, (usually 1–2 mm. in cross section and 20–30 crystals in 1 c.c.), and we can clearly observe its usual arrangement of the particles of carbonaceous matter. Ordinarily, the developed face of the crystal is only ∞P. Besides the crystals, black spots are also observed. Under the microscope, the general ground mass is seen to consist of a large amount of carbon particles and pleochroic biotite flakes. The inner structure of the chiastolite crystals is found to have been changed into fibrous, or scaly muscovite-like aggregation, which is enclosed by brown biotite flakes, and some of the crystals to have undergone the decomposition into unresolvable aggregations with vivid polarization color. The spots consist of carbon particles, biotite flakes and transparent mineral in equal quantities, as in the spotted clay slate. The zones belonging to this rock are as follows:

Dike A, 1. . . . 30 cm. in thickness.
„ „ 11. . . . 70 cm. „ „
„ B, 2. . . . 35 cm. „ „
„ „ 9. . . . 45 cm. „ „

The last zone consists of large crystals of chiastolite. The cross-section of the largest crystal is measured to be 3 mm., by 2–3 cm. in length, and it contains 10 crystals in 1 c.c.

Dike B, 12. . . . 45 cm. in thickness.

In this zone small, perfect crystals of chiastolite occur; 1 in 2 c.c.

Dike B, 13. . . . 1 m. in thickness.

The crystals are more numerous in this zone, and the largest has been found to be 2 mm. in cross-section.

Dike B, 14. . . . 90 cm. in thickness.

In this zone the crystals are still larger, being 4 mm. in cross-section, and 1 in number in 1 c.c.

Imperfect Cerasite Clay Slate.

It is a dark-greyish compact rock, the grey shade being considerably deeper than in the two rocks already described. Formless minerals (5 mm. in cross-section) with micaceous aspect, are developed in this rock, as are usually observed in the *aureola* in other metamorphosed regions. Under the microscope, newly formed biotite is seen to be scattered over the general ground mass. This micaceous mineral consists of carbon particles, biotite and transparent mineral aggregations in orderless manner. When we examine this mineral under crossed nicols, it exhibits more or less radial orientation, and seems to separate into six sections; therefore it may be considered as the cerasite of an imperfect growth. The zones belonging to this rock are as follows:

Dike A, 2. . . . 70 cm. in thickness.
„ „ 12. . . . 12 cm. „ „
„ B, 3. . . . 5 cm. „ „
„ „ 10. . . . 35 cm. „ „

Chiastolite Clay Slate.

This rock consists of black and grey bands, (2–3 mm. in thickness) and chiastolite crystals; and small spots are observed in the black bands, as in the spotted chiastolite clay slate. Under the microscope, it is seen to consist of two parts; one of which contains abundant biotite and few carbon particles, the other little biotite and many carbon particles. The former is undoubtedly the metamorphosed sandy portion, no development of any other new minerals being observed and the latter the metamorphosed clayey portion, as in many cases previously described. Besides the large, distinct crystals, which are more or less decomposed, as in the previously mentioned cases, there are a few small, fresh, lath-shaped crystals, which are macroscopically observed as black spots. The fresh crystals differ from the large ones, and contain many carbonaceous particles along the longer direction, leaving narrow, transparent parts on both sides; under crossed nicols, they are shown to be wholly crystalline, with vivid polarization color, just like those found at Usuginu in Rikuchiu province. In general appearance, this rock resembles spotted chiastalite clay slate. The zones belonging to this rock are as follows:

Dike B, 4. . . . 30 cm. in thickness.
„ „ 5. . . . 25 cm. „ „

The last is a clay slate zone, divided into two parts by a fault: the bank side consists of imperfect cerasite clay slate, while the river side of the chiastolite clay slate.

Metamorphosed Sandstone.

It is a granular, light violet-grey rock, having no predominant minerals. Under the microscope, it is seen to consist of many quartz grains and small biotite flakes, with here and there spots of carbon particles. The zones allied to this rock, are as follows:

Dike A, 2.	. . .	3 cm.	in thickness.
„ „ 6.	. . .	1 m.	„ „
„ „ 8.	. . .	35 cm.	„ „
„ „ 10.	. . .	75 cm.	„ „
„ B, 6.	. . .	1 m.	„ „
„ „ 11.	. . .	45 cm.	„ „
„ „ 15.	. . .	60 cm.	„ „
„ „ 17.	. . .	10 cm.	„ „
„ „ 19.	. . .	10 cm.	„ „

Cerasite-Chiastolite Clay Slate.

It is a very fine granular, light violet-grey rock, like metamorphosed sandstone. It contains large green crystals of cerasite and small spots. Under the microscope, it is seen to consist of abundant biotite, quartz grains and small magnetite grains. The cerasite is found to have completely altered to a pinite-like, green mineral, wholly analogous to that of the Kameoka region. Y. Kikuchi identified this pseudomorphous mineral as chlorophyllite. The small spots are fresh chiastolite crystals, with lath-like or rhomboidal sections scattered over with many carbon particles, especially at the margin of the crystals. This rock occupies only the zone 4, dike A, (thickness 25 cm.).

Cerasite Clay Slate.

This rock differs from cerasite-chiastolite clay slate simply in the absence of chiastolite, but the dimensions of the cerasite crystals are larger and vary in each zone. The natural figures on the rock surface are same as those found in Kikuchi's description. The transverse sections exhibit hexagonal figure divided into six sections, while the longitudinal sections a rectangular form, and are interrupted by two diagonal lines, the boundaries of which are filled up with white quartzose materials. The zones belonging to this rock are as follows:

Dike A, 5.	. . .	35 cm. in thickness.
„ „ 7.	. . .	15 cm. „ „
„ „ 9.	. . .	30 cm. „ „
„ B, 16.	. . .	10 cm. „ „
„ „ 18.	. . .	10 cm. „ „

Mikanohara Region.

Here also the paleozoic rocks are pierced by many granite dikes, and contact phenomena are observed like those described of the Watsuka region. All metamorphosed rocks in this region exhibit more or less schistose structure. Hornstone is found to have been converted into quartzite with abundant biotite, sandstone into mica schist, and clay slate into micaceous slate accompanied by new minerals. Chiastolite occurs here and there in metamorphosed clay slate. In Furubashi, large, well defined white crystals of chiastolite imbed in black clay slate, locally called *Hashira-ishi* (columnar stone). Cerasite and chiastolite sometimes occur together in one and same rock. In such a case, chiastolite is shaded with a pink color and seldom contains carbon particles; while cerasite alters into pinite-like green mineral. Tourmaline is present in small needles in black clay slate, thus we have the evidence of the introduction of a small quantity of volatile constituents from the granite. Though we cannot determine the stratigraphical order in this region, we can observe the occurrence of chiastolite and cerasite by the contact action.

Conclusion.

The late Y. Kikuchi explained the occurrence of both minerals, stating that it may depend upon the chemical nature of the clay slate as well as upon that of the granite which exerts the action of metamorphism; and he assumed that clay slate may produce cerasite by biotite granite, and chiastolite or andalusite by

hornblende granite. His assumption, however, seems to be disproved by the facts observed by the author. Last year, in Koya village, near Funaya, the author found beautiful chiastolite crystals produced in clay slate by the contact of ordinary biotite granite, and again afterwards, two minerals in the Watsuka region, where they are developed either in one and same clay slate or different ones by the action of a granite. These facts are most interesting concerning the origin of those minerals. If, the metamorphosed rocks are to be examined, their different natures can readily be noticed. Thus, cerasite clay slate is always tinged with a violet-grey color and fine granular, while chiastolite clay slate is always black, compact and fissile. By the aid of the microscope, it is found that the former contains much biotite and quartz grains, while the latter little biotite and abundant carbon particles. When they occur in the same rock, the crystals of chiastolite are always smaller than those of cerasite. Sandstone is found to have produced many biotite flakes, and its color to have changed to a violet-grey, closely resembling cerasite clay slate with respect to those metamorphic phenomena, but there is no production of other minerals. It is, therefore, necessary to conclude that the occurrence of the minerals is no doubt due to the clayey or sandy construction of the clay slate, effected by the physical action of the granite. That is to say, chiastolite is produced in the pure clay slate and cerasite in the sandy. As to the occurrence of both minerals in one and same clay slate, it can only be assumed that the original rock was a sandy clay slate, with clayey patches scattered through it.

February, 1905.

Retardation Tests with an Unloaded, Covered Railway Wagon.

By

Sakurō Tanabe.

A series of retardation tests with an unloaded railway wagon on the Kwansai Railway Company's line near Kamo Station, were made some time ago by the author in collaboration with Mr. T. Hibi. The day was clear, the average temperature of the air was 67° Fahr. in the shade, and there was no wind. The wagon weighed 5·15 tons; the body was 18 feet 8¾ inches long, 7 feet 3 inches wide, and 6 feet 6 inches high; the area of the cross-section being 46 square feet. The rigid wheel base was 9 feet ¼ inch. The wheels were 33 inches in diameter, and had steel tyres. The rails were of Vignole's shape, weighed 60 pounds to the yard, and were laid upon wooden sleepers to a 3 foot 6 inch gauge.

To the body of the wagon we attached a wooden piece carrying a small brass plate electrically connected with a wheel and axle of the wagon. By side of the line, and ranged along it at intervals of 20 feet, was laid a series of wooden rods, each rod being ½ inch thick, 2 inches wide, and 3 feet long, and provided with a brass plate ½ inch wide, $^1/_{16}$ inch thick, and 6 inches long, at the end which projected toward the line.

Away from the railway we laid a smoked cylinder which was revolved by clockwork. Upon the cylinder there were two pens; one of which, worked by a pendulum, registered the time, while the other, attached to a magnet, recorded the instant when the rod on the wagon struck the brass plates laid by the side of the line.

The wagon was pushed by a locomotive moving at a different rate of speed for each test, and when sufficient momentum had been imparted, the locomotive was suddenly stopped and the wagon was allowed to run by inertia. The record of the time of transit over each of the 20 feet sections was accurately obtained on the diagrams of the smoked cylinder.

If there were no rotating part in the wagon, the potential height due to the velocity would be

$$y = 0{\cdot}033445\,V^2$$

where y is the potential height in feet and V is the velocity of the wagon in miles per hour. But because the wagon has wheels and axles which rotate, the constant should be modified. In our case we obtained

$$y = kV^2 \text{ where } k = 0{\cdot}03905 \quad . \quad . \quad . \quad (1)$$

From the observed velocities at different points, the corresponding potential heights were calculated by the formula (1). The railway line was not theoretically level, either longitudinally or crosswise, and it was necessary to reduce all consequent errors in order to obtain the curve of potential heights of the running wagon. The horizontal distance in feet being represented by x, the equation,

$$y = ax^3 + bx^2 + cx \quad . \quad . \quad . \quad . \quad . \quad (2),$$

where $a = 0{\cdot}000\ 000\ 000\ 4216$,

$b = 0{\cdot}000\ 000\ 6325$,

$c = 0{\cdot}000\ 9192$.

gives very close coincidence with the actual observed values. The velocity range of the experiments was up to 25 miles per hour.

The resistance of the wagon against running being the differential coefficient of y with respect to x, in order to represent it in pounds per ton of 2000 pounds, we have to multiply the coefficient by 2000. Representing the resistance by R, the following equation is obtained

$$R = Ax^2 + Bx + C \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $A = 0{\cdot}000\ 00253$,

$B = 0{\cdot}00253$,

$C = 1{\cdot}838$.

Eliminating x and y from these three equations, the relation between R and V is

$$R=A\left\{\sqrt[3]{-\frac{r}{2}+\sqrt{\frac{r^2}{4}+q^3}}+\sqrt[3]{-\frac{r}{2}-\sqrt{\frac{r^2}{4}+q^3}}-\frac{b}{3a}\right\}^2$$
$$+B\left\{\sqrt[3]{-\frac{r}{2}+\sqrt{\frac{r^2}{4}+q^3}}+\sqrt[3]{-\frac{r}{2}-\sqrt{\frac{r^2}{4}+q^3}}-\frac{b}{3a}\right\}$$
$$+C \quad . \quad . \quad . \quad . \quad (4),$$

$$\text{where } r=\frac{2b^3}{27a^3}-\frac{cb}{3a^2}-\frac{k}{a}V,$$
$$3q=\frac{b^2}{3a^2}+\frac{c}{a}.$$

Such a value of R being too complicated, it is better to find an approximate value in a much simpler form. The equation

$$R=2+0{\cdot}4V+0{\cdot}04V^2,$$

though simple in form, gives close approximation to the observed relationship between R, the resistance in pounds per ton of 2000 pounds, and V, the velocitiy of the wagon in miles per hour. The last factor of the above equation, namely $0{\cdot}04V^2$, is nearly equal to the resistance due to the atmosphere, leaving the former two, $2+0{\cdot}4V$, as the rolling resistance only of the unloaded covered railway wagon.

February, 1905.

On the Electromagnetic Screening Effect of Metallic Conductors.

By

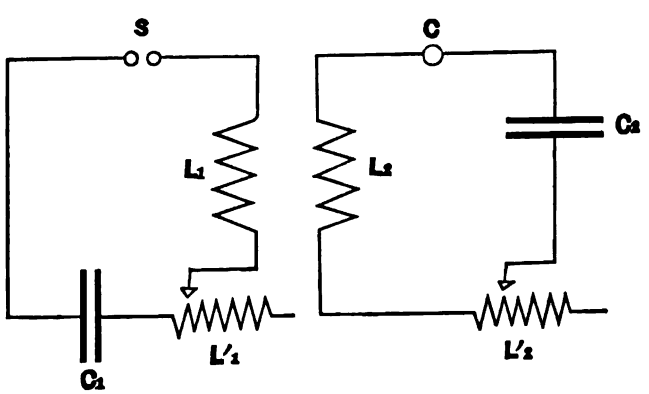
Kunito Ogawa.

Consider a metallic circuit subjected to the action of oscillatory electromagnetic disturbances. If a conductor be placed in front of the circuit so as to shield it from the train of impinging disturbances, the screening effect of that conductor depends upon and increases with the frequency of the oscillations and the electric conductivity of the conductor.

The object of this paper is to put forth the results obtained experimentally with regard to the screening action of simple metallic loops and thin metallic foils.

The arrangements taken in the experiments are shown in Fig. I. The source of the oscillatory electromagnetic disturbances is a Leyden jar C_1, a coil L_1, together with an adjustable self-induction L'_1, and a spark gap S. In front of this circuit,

Fig. I.



there is a secondary circuit consisting of a coil L_2, a calorimeter C, a Leyden jar C_2, and an adjustable self-induction L'_2.

The calorimeter is composed of a small glass bulb with a stop-cock and with an U shaped capillary tube partly filled with pure water, as shown in Fig. II. A wire of small cross-section is stretched across lengthwise within the bulb, and this wire forms a portion of the secondary circuit.

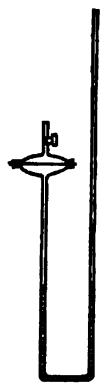


Fig. II.

Now, when the primary circuit is excited by means of an induction coil, whose poles are connected with the armatures of the jar C_1, and when electric oscillations of a certain period occur, the secondary circuit responds to the forced oscillations provided the electric constants of the circuit are properly chosen, and then we have the so-called electric resonance. This electric resonance can be produced by means of the adjustable self-induction L'_2, the capacity of the jar C_2 being properly taken beforehand.

The occurrence of the resonance is indicated by the maximum rise of the water column in the capillary tube in consequence of the heating effect of the resonance current.

Let i be the continuous steady current which would produce the same thermal effect as the oscillatory resonance current in the secondary current does.

If then i_1 and i_2 be respectively the values of the above steady current corresponding to the resonance current before and after a metallic loop or conductor is interposed between the primary and the secondary circuits, the ratio $\frac{i_2}{i_1}$ would express the screening effect of the loop or of the conductor. In the other words, the smaller the ratio $\frac{i_2}{i_1}$ the greater the screening effect.

In the experiments, i_1 and i_2 were measured by sending a direct constant current from an accumulator through the secondary circuit. The capacity and self-induction of the secondary circuit were experimentally determined, and from their values, the period T, and consequently the frequency n of the electric oscillations, was calculated by the formula

$$T = 2\pi\sqrt{LC}.$$

The following tables give the results of the observations:

I. Copper Loops.

$n = 1577 \times 10^3$

Current in Amp.		Screening Effect.	Resistance of Loops in Ohms.
i_1	i_2	$\frac{i_2}{i_1}$	
0·330	0·203	0·615	0·004
0·330	0·213	0·654	0·009
0·330	0·223	0·676	0·020
0·330	0·232	0·703	0·049
0·330	0·238	0·721	0·124
0·330	0·244	0·739	0·152
0·330	0·249	0·754	0·262
0·330	0·259	0·785	0·722

$n = 922 \times 10^3$

Current in Amp.		Screening Effect.	Resistance of Loops in Ohms.
i_1	i_2	$\frac{i_2}{i_1}$	
0·293	0·195	0·665	0·004
0·293	0·203	0·693	0·009
0·293	0·213	0·727	0·020
0·293	0·223	0·761	0·049
0·293	0·231	0·788	0·124
0·293	0·238	0·812	0·152
0·293	0·245	0·836	0·262
0·293	0·249	0·850	0·722

$n = 235 \times 10^3$

Current in Amp.		Screening Effect.	Resistance of Loops in Ohms.
i_1	i_2	$\frac{i_2}{i_1}$	
0·303	0·234	0·772	0·004
0·303	0·243	0·802	0·009
0·303	0·248	0·818	0·020
0·303	0·254	0·838	0·049
0·303	0·259	0·855	0.124
0·303	0·262	0·865	0·152
0·303	0·265	0·875	0·262
0·303	0·267	0·881	0·722

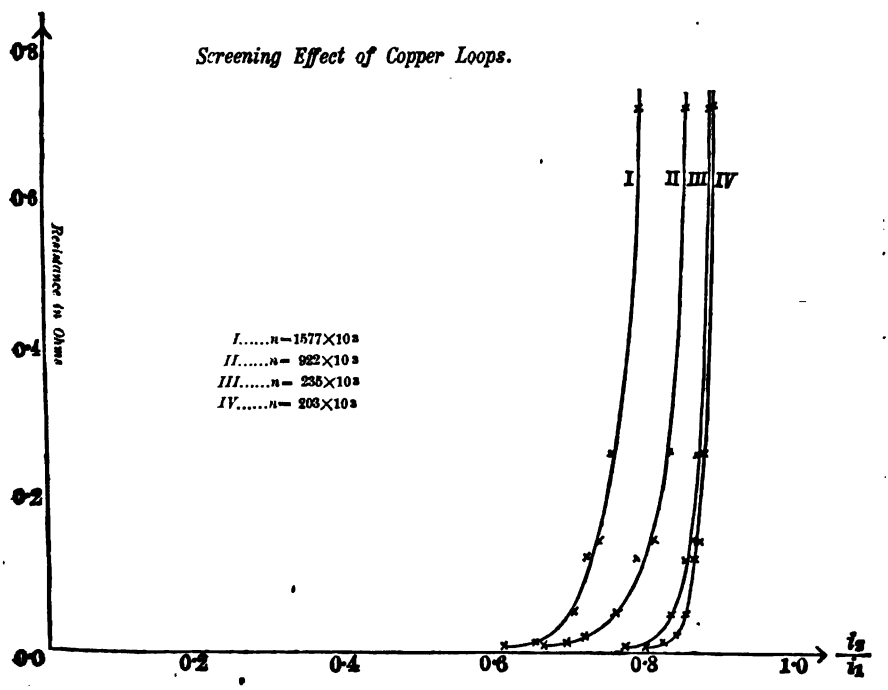
$n = 203 \times 10^3$

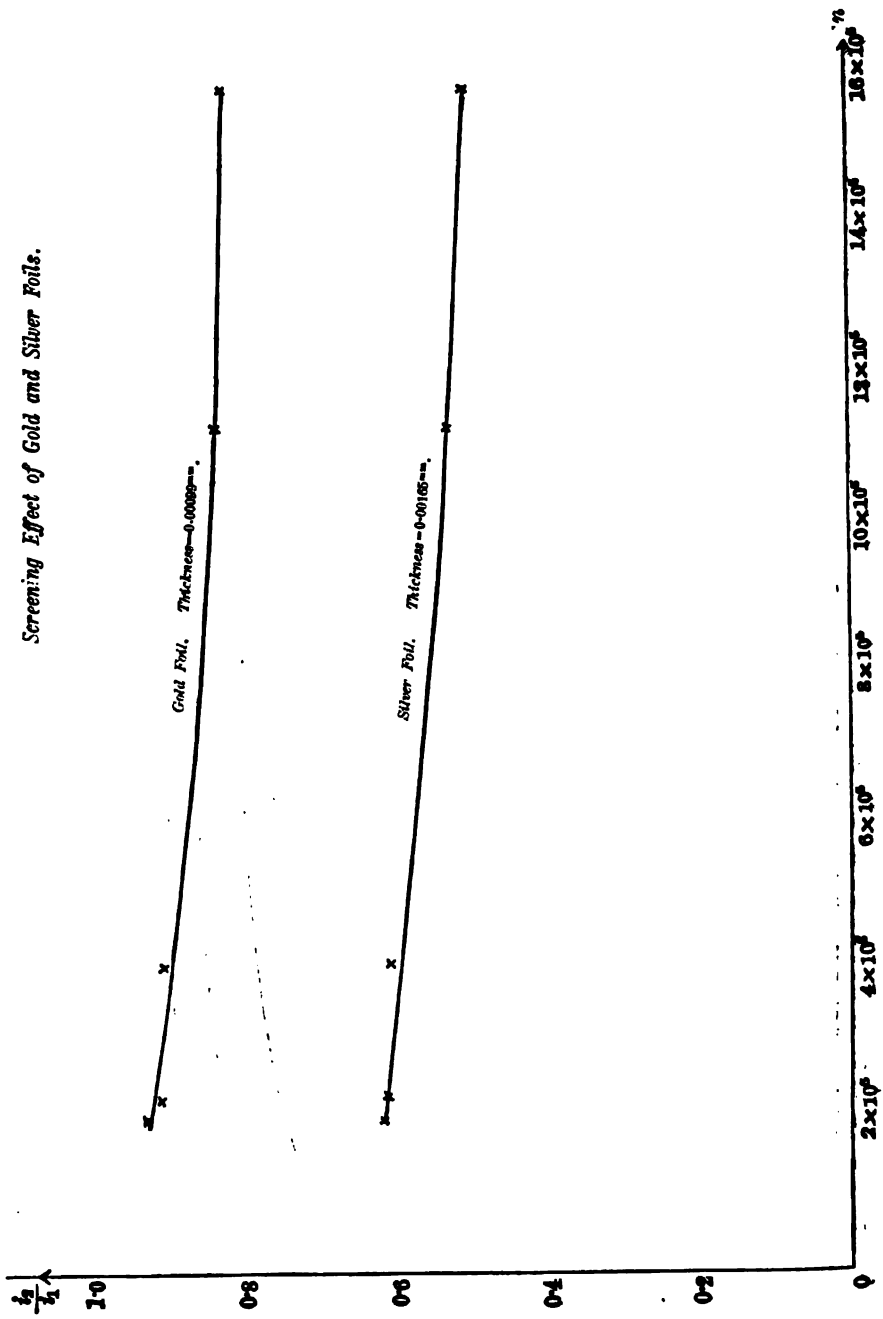
Current in Amp.		Screening Effect.	Resistance of Loops in Ohms.
i_1	i_2	$\frac{i_2}{i_1}$	
0·364	0·291	0·799	0·004
0·364	0·300	0·824	0·009
0·364	0·306	0·841	0·020
0·364	0·311	0·854	0·049
0·364	0·315	0·865	0·124
0·364	0·318	0·874	0·152
0·364	0·319	0·876	0·262
0·364	0·321	0·882	0·722

II. Gold and Silver Foils.

	Gold Foil. Thickness = 0·00099 mm.				Silver Foil. Thickness = 0·00165 mm.		
Frequency.	Current in Amp.		Screening Effect.	Frequency.	Current in Amp.		Screening Effect.
n	i_1	i_2	$\frac{i_2}{i_1}$	n	i_1	i_2	$\frac{i_2}{i_1}$
1577×10^3	0·320	0·263	0·819	1577×10^3	0·320	0·162	0·506
922×10^3	0·315	0·262	0·832	922×10^3	0·315	0·167	0·530
411×10^3	0·315	0·287	0·910	411×10^3	0·310	0·189	0·610
235×10^3	0·310	0·284	0·916	235×10^3	0·310	0·191	0·617
203×10^3	0·303	0·282	0·931	203×10^3	0·310	0·192	0·619

Plotting the above results, we get the following curves:




Screening Effect of Gold and Silver Foils.
Gold Foil. Thickness=0.00009cm.
Silver Foil. Thickness=0.00165cm.
$\frac{i_2}{i_1}$
1·0
0·8
0·6
0·4
0·2
0
2×10⁵
4×10⁵
6×10⁵
8×10⁵
10×10⁵
12×10⁵
14×10⁵
16×10⁵
%

Action of Alcohol upon Mercury Perchlorates.

By

Masumi Chikashige.

I. GENERAL CONSIDERATION.

Concerning the action of alcohol upon the hydrated mercuric perchlorate, $Hg(ClO_4)_2 \cdot 6H_2O$, we have an early account by Serullas.[1] Since that time there had been no one who attempted further investigation of this subject till 1895, when the author published an article on mercury perchlorates[2], in which he gave some new statements respecting it. As to the behaviour of the hydrated mercurous perchlorate, $Hg_2(ClO_4)_2 \cdot 4H_2O$, when acted upon by alcohol, we cannot find any account hitherto, excepting that given by the author, which is contained in the same article just referred to. All those statements being, however, merely qualitative and not exact, the author has been led to make more minute and precise investigations into the behaviours of these salts when treated with alcohol, and in the course thereof he has been able to discover some new reactions arising from those compounds.

The fact that the hydrated mercuric perchlorate, when treated with cold alcohol, goes into solution, leaving a white, insoluble compound which is easily decomposed by water, had already been described by Serullas, and confirmed by the author. He has therefore attempted in this opportunity to determine the exact composition of that insoluble compound; but as it has soon been found that such a compound can be obtained in a very small

[1] Ann. Chim. Phys., [2], **45**, 270; **46**, 294, 323.

[2] Jour. Chem. Soc., **67** (1895), 1013.

quantity only, and, moreover that if the solution containing this compound be boiled, it would dissolve giving way to the precipitate of a different nature, he has not been able to find out any experimental data for its composition. By inference, however, drawn from a similar substance obtained from the mercurous salt when treated with cold alcohol, we can bring forward the explanation on the assumption that it is the anhydrous mercuric perchlorate, perhaps got somewhat basic through the loss of acid. In spite of the presence of this compound, the alcoholic solution having been boiled to a certain extent, a considerable amount of a white, flocculent precipitate made its appearance as has just now been stated. On continuing to boil the solution, this precipitate was found to have been converted gradually into a coarse granular form, which sank to the bottom of the flask. This last precipitate then remained unchanged, even when the boiling with alcohol was continued. During the reaction, the alcohol was found to have been copiously oxidised into aldehyde, as was distinctly noticed by its characteristic odour. The fact that these two precipitates varied considerably in amount, acccording to the samples of the mercuric salts originally taken, has led the author to conclude at once that there exists a new basic salt, *hydrated monoxy-trimercuric tetraperchlorate*, having the composition $Hg_3(ClO_4)_4O \cdot 12H_2O$, from which he has always been able to obtain a greater amount of the precipitates. On analysis, the first variety of the precipitates was found to be a basic salt, *monoxy-dimercuric diperchlorate* with the composition $Hg_2(ClO_4)_2O$, while the second proved to be *dioxy-trimercuric diperchlorate*, $Hg_3(ClO_4)_2O_2$. These two basic compounds are explosive in their nature, especially more so in the case of the latter. It is also very interesting to note that the latter is isomeric with the so-called *oxymercuric perchlorate*, $Hg_3(ClO_4)_2O_2$, previously discovered by the author[1], and observed to be highly stable in its behaviour towards heat:

[1] *Loc. cit.*

he now proposes to distinguish these two isomers from each other by designating the old one as *α*– and the new one as *β–dioxy-trimercuric diperchlorate.*

Now, the filtrate from these precipitates will contain principally the mercurous salt mixed with a little of the mercuric. If the case taken at the start be that of the normal mercuric salt, the precipitation of those two basic compounds is often so very small as to be practically negligible, and the filtrate will contain the mercurous salt up to 91 – 92 per cent. of the original perchlorate used, the rest being in fact nearly all the mercuric salt unchanged. It has been found by Ray[1] that mercurous nitrite, when treated with water, tends to form a double salt, $2HgNO_2 \cdot 4Hg(NO_2)_2$, and that the decomposition is stopped when it goes so far as 78 per cent. of the original salt. It is possible that such a sort of reaction occurs in the present case though in the opposite sense, giving rise in the solution to a double compound, probably having such a composition as $9Hg_2(ClO_4)_2 \cdot 2Hg(ClO_4)_2$. In fact, on slow evaporation over a water-bath, there are obtained gray, needle-shaped crystals whose composition is found, on analysis, to correspond approximately with the formula above shown. Serullas states that, on evaporation, the alcoholic solution of mercuric perchlorate gives both the mercurous and mercuric salts, being accordant with the results of the author's experiments.

Now, such alcoholic solution, at first obtained perfectly clear, becomes milky in the course of a few days through the formation of a precipitate, more or less explosive, which is probably derived from the decomposition of the remaining mercuric perchlorate; because the mercurous salt itself is, as will be shown later, remarkably stable in the alcoholic solution. The small quantity of aldehyde retained in the solution might also give rise to the production of thc precipitates, because only a few c.c. of acetaldehyde, intentionally mixed with the solutions of both the mercuric and mercurous salts, at once effected the separation of precipitate which at first looks white but gradually turns to

[1] Jour. Chem. Soc., **71** (1897), 340.

gray. The precipitate consists, in fact, of the β-oxymercuric salt mixed with a variable quantity of metallic mercury, and will be specially treated in the later chapter.

Just as the author's observation on the formation of the oxymercuric and mercurous compounds, a similar case of decomposition has recently been described by Ray[1], who studied the behaviour of mercuric nitrite when heated to 100°, and found that the decomposition takes place in two ways; namely, on the one hand so as to give the oxymercuric compound, and on the other the mercurous compound. It is therefore obvious that the action of alcohol upon the mercuric salt will generally go on in two different directions; firstly, to make it less oxidised; and secondly, to make it more so. The mechanism of the reaction proceeding in the present instance may therefore be formulated in the following manner:

1. $$\begin{matrix} Hg<^{ClO_4}_{ClO_4} \\ Hg<^{ClO_4}_{ClO_4} \end{matrix} \longrightarrow \begin{matrix} Hg<^{ClO_4} \\ Hg<_{ClO_4} \end{matrix} .$$

2. $$\begin{matrix} Hg<^{ClO_4}_{ClO_4} \\ Hg<^{ClO_4}_{ClO_4} \end{matrix} \longrightarrow \begin{matrix} Hg<^{ClO_4} \\ O \\ Hg<_{ClO_4} \end{matrix} .$$

3. $$\begin{matrix} Hg<^{ClO_4}_{ClO_4} \\ Hg<^{ClO_4}_{ClO_4} \\ Hg<^{ClO_4}_{ClO_4} \end{matrix} \longrightarrow \begin{matrix} Hg<^{ClO_4} \\ O \\ Hg<_{O} \\ Hg<_{ClO_4} \end{matrix} .$$

The fact that the last two reactions are far more easily induced in the case of monoxy-trimercuric tetraperchlorate, may be ascribed to its basic character originally retained and the mechanism of the reactions cannot be so far apart from that above shown.

[1] Jour. Chem. Soc., 85 (1904), 523.

As to the behaviour of the perchloric acid radical itself, it may be said that several complex decompositions are involved, the principal of which being, perhaps, the formation of perchloric ether. Though it is difficult, as stated by Roscoe[1], to obtain this ether by the direct action of perchloric acid upon alcohol, owing to its high explosibility, yet we find in some of the larger works on Chemistry a statement that, to some extent, it may thus be brought into existence. Moreover, it is stated by Hare and Boyle[2] and confirmed by Roscoe[3], that the ether can easily be obtained from a salt of perchloric acid by treating it with a certain ethyl compound. Taking all these cases into consideration, it can hardly be denied that the direct action between normal mercuric perchlorate and alcohol is, on the one hand, simply to deprive the acid radical of the salt, and to give rise to the formation of the mercurous salt; while on the other, perchloric ether, so highly oxygenated, is partly decomposed by heat so as to form aldehyde and also the oxymercuric perchlorates. Reduction of the perchloric acid radical seems, however, in any case not to progress so far as to form hydrochloric acid: this becomes obvious from the fact that no trace of mercurous chloride precipitated during the reaction can be found. Even on the continued evaporation of the alcoholic filtrate, the compounds precipitated do not contain *chlorides* at all. Some other experiments to determine the stability of perchloric acid against reducing agents, have been undertaken and the results will be given in detail in the experimental part hereof.

We shall now consider the case in which mercurous perchlorate is treated with alcohol. The author has stated in his previous paper that it is decomposed into soluble acid salt and white basic salt. He now finds that it is, for the greater part, dissolved in the solvent, only a small part of it being converted into a white compound not essentially differing in its external

[1] Jour. Chem. Soc., **15** (1862), 213.
[2] Phil. Mag., **19**, 370.
[3] *Loc. Cit.*

appearance from the original crystals. The latter compound, when washed with water, is at once decomposed into a gray substance which gradually forms the metallic globules of mercury. It is, however, very stable in alcohol, unless it is continuously boiled, when it becomes dissolved, leaving practically no residue at all. On analysis, it was found to contain about 63 per cent. of mercury and hence should be mercurous perchlorate, losing much of its water of crystallisation (theory requiring 66.7 per cent. of mercury). The fact that the hydrated mercurous perchlorate loses its acid and water to some extent over sulphuric acid, has already been ascertained by the author, and now the same phenomenon seems to happen in the alcoholic solution. The latter solution, filtered if turbid, keeps very well, showing no sign of decomposition for a considerable period of time. As is well known, Rose holds strongly that a mercurous compound does not form any basic salt, and that what is usually called a basic one, is in fact an admixture of the mercuric salt and mercury formed by the dissociation of the original compound. The wonderful stability of the mercurous perchlorate now observed, may be taken as the strong evidence for the confirmation of Rose's view; because, if the alcohol tends to make the salt basic, the latter would then be dissociated in the following way:—

$$\begin{array}{c} Hg—ClO_4 \\ | \\ Hg—ClO_4 \end{array} \longrightarrow Hg + Hg\left\langle\begin{array}{l} ClO_4 \\ ClO_4 \end{array}\right. ,$$

but as the mercuric salt now formed has, as already stated, a great tendency to be reduced back to the original state of combination, it naturally follows that the mercurous salt is not easily acted upon by alcohol; while if it should happen to be acted upon, it would form highly mercuriferous compounds and give the gradual precipitation of metallic mercury. Such is in fact the case when the clear alcoholic solution of mercurous perchlorate is evaporated over a water-bath.

II. EXPERIMENTAL PART.

1. HYDRATED MONOXY-TRIMERCURIC TETRAPERCHLORATE,

$$Hg_3(ClO_4)_4O \cdot 12H_2O.$$

Instead of dissolving mercuric oxide in an excess of aqueous perchloric acid, we may make the latter over-saturated with the former by adding to such an excess as there will still be left some of it uncombined. When such a solution, after filtering through asbestos, is evaporated over a water-bath to a sufficient degree of concentration and allowed to cool in a desiccator, there are formed white, prismatic crystals, much resembling the ordinary mercuric perchlorate in their appearance, excepting only that they appear to be rather more opaque than the ordinary ones. After separating such crystals from the mother liquor and drying them perfectly on a porcelain tile, they were found to be soluble in water without leaving a considerable amount of the deposit of yellow oxide of mercury: the content of mercury has been determined as sulphide, in exactly the same way as is stated in the author's previous paper, which has already been referred to. The results are as follows:—

	Found.	Calc. for $Hg_3(ClO_4)_4O \cdot 12H_2O$.
Mercury	48·80	48·76

On evaporation, the aqueous solution of this basic salt gives a gradual deposition of mercuric oxide and finally the crystals of the ordinary perchlorate. When treated with alcohol, it gives two different basic salts, as already stated in the general consideration.

2. THE SUBSTANCE OF THE PROBABLE COMPOSITION,

$$9Hg_2(ClO_4)_2 \cdot 2Hg(ClO_4)_2.$$

How the ordinary hydrated mercuric perchlorate will behave when treated with alcohol, has already been stated. Now, when

the clear alcoholic solution of it has been obtained after sufficient boiling, it is treated with hydrochloric acid in order to effect the precipitation of mercurous chloride. On testing with hydrogen sulphide, the filtrate from the chloride always shows the presence of a small amount of the unchanged mercuric salt. The quantity of the mercurosum present has been determined by weighing the precipitated chloride and been compared with the total amount of mercury contained in the original salt. The results are as follows :—

	Found.			Total mercury in the original salt.
	I.	II.	III.	
Mercurosum	35·9	35·1	36·2	39·47

So it is obvious that about 91 – 92 per cent. of the mercury in the original salt has been converted into the mercurous state; some of the rest having been precipitated as basic salts and some being still in the form of mercuricum. When the alcoholic solution is diluted with a certain quantity of water and then evaporated to a suitable concentration, it gives chiefly a crop of the ordinary hydrated mercurous perchlorate crystals in the form of large plates. If, however, such a solution is subjected to evaporation without any previous addition of water, the result presents itself under a totally different aspect. Placed over a water-bath, briskly boiling, the solution after a while becomes decomposed into a black residue, consisting chiefly of metallic mercury and basic mercurous perchlorates. If, on the other hand, the temperature of the bath is kept very low, the alcohol slowly evaporates, and the solution finally reaches the point when it gives fine needle-shaped crystals of slightly gray colour, owing to the presence of reduced mercury. These crystals, collected and dried, were immediately subjected to analysis. The aqueous solution, of course, contained a certain quantity of undissolved mercury, which was separated by filtration; the mercurosum was determined as chloride, and the perchlorate radical as the potassium salt using a different sample and after removal of the mercury :—

	Found. I.	Found. II.	Calc. for $9Hg_2(ClO_4)_2 \cdot 2Hg(ClO_4)_2$.
Mercury	62·37	—	64·63
Perchlorate radical	—	34·80	35·36

These results are not much in accordance with the composition expressed by the formula, and this may evidently be ascribed to the difficulty of getting such a compound in a perfectly pure state. The author has further attempted to prepare it in a purer form, both by evaporating the solution *in vacuo* and by placing it for a long period of time over calcium chloride. The trials have, however, shown that it is almost impossible to obtain a better result.

3. MONOXY-DIMERCURIC DIPERCHLORATE,

$$Hg_2(ClO_4)_2O.$$

When the precipitation of the white, flocculent basic salt was assumed to have reached the maximum quantity, the boiling of the alcoholic solution of the hydrated basic mercuric perchlorate was discontinued and the precipitate was filtered, washed well with water, and dried in a steam-bath. In addition to the fact that the total yield was very small, it was extremely difficult to hit just the exact moment when all the precipitate had acquired the same degree of basicity. Dissolved in aqua regia, the content of mercury was determined, with necessary precautions, as sulphide. The result gave 60·35 per cent. and is not concordant with the quantity expected from the formula $Hg_2(ClO_4)_2O$, which amounts to 65.04 per cent. It dissolves neither in water nor in acids, excepting aqua regia. Heated over a Bunsen flame, it is tolerably stable, remaining unaffected until it nearly reaches a dull red heat; then it is suddenly decomposed, causing a slight explosion, when it burns with feeble violet flame and leaves the residue of red mercuric oxide. The phenomenon reminds us of mercury fulminate, but, of course, is far milder than that of the latter.

4. β-DIOXY-TRIMERCURIC DIPERCHLORATE,

$$Hg_3(ClO_4)_2O_2.$$

The white granular precipitate formed when the alcoholic solution of the hydrated basic mercuric perchlorate is boiled as long as the decomposition is noticed, was filtered off, washed with water and dried in the same way as in the last case. Dissolved in aqua regia and analysed with necessary precautions, it gave the following result:—

	Found. I.	Found. II.	Calc. for $Hg_3(ClO_4)_2O_2$.
Mercury	70·73	71·15	72·13

It is a stable, white powdery substance, insoluble both in water and in acids, and violently explosive at high temperatures. Heated to dull red heat, even a very small quantity instantly detonates with a loud report, and nothing at all is left. In one case, only a milligram or so of it was brought to the temperature of dull redness, when there took place such a violent explosion that the end of a nickel spatula, which had been used in the experiment, was entirely distorted and to some extent broken. Such detonation may be produced by percussion also. Compared with about an equal quantity of mercury fulminate, its explosibility is certainly far more energetic, while its stability at a temperature below dull redness shows no less than the former. Contemplating its use in percussion-caps, the author took 37·5 parts of this salt and the same quantity of potassium chlorate with 25 parts of antimony sulphide, as is usually done in the case of the fulminate-caps, and mixed them thoroughly together with a small quantity of gum-solution. In reality, this mixture could be practically used for ordinary gunpowder priming.

It is very interesting to note that both the α- and β-varieties of dioxy-trimercuric diperchlorate are very stable, each being the final product arrived at when the hydrated mercuric perchlorate is acted upon by heat or by alcohol under certain limited

conditions. They possess, however, certain inherent differences in that the α-variety is very quietly decomposed above the temperature at which mercuric oxide is freely decomposed, and also in that it is decomposed by water into soluble mercuric perchlorate and mercuric oxide which remains undissolved. They are certainly isomeric to each other, the differences just shown arising naturally from the varying conditions accompanying their modes of formation.

5. REDUCTION OF MERCUROUS PERCHLORATE IN ALCOHOLIC SOLUTION BY ACETALDEHYDE.

It has already been stated that the clear alcoholic solution of mercurous perchlorate mixed with a little of the mercuric salt, will gradually give a precipitate more or less explosive in its nature. This precipitate, when collected and dried, had a somewhat grayish appearance and proved to be insoluble in water and in acids. On analysis, it was found that its composition is not constant, yet more mercuriferous than the normal mercuric salt. The author's view as to the cause of the formation of such a precipitate have already been given hereinbefore. Experiments with acetaldehyde have been made in order to ascertain whether the aldehyde may also give rise to the production of that precipitate or not. The precipitate formed in the alcoholic solutions, which was obtained both from the mercurous and the mercuric salts, was collected on filter paper, washed and dried. It is violently explosive and insoluble either in water or in acids, excepting aqua regia. It has a grayish appearance through the liberation of mercury, and no definite composition. Selecting, however, the portions having as much of the white appearance as possible, its content of mercury was determined as usual, the results being as follows:—

	Found.		Calc. for
	I.	II.	$Hg_3(ClO_4)_2O_2$.
Mercury	73·90	73·35	72·13

These results point approximately to the composition of the

β-oxymercuric salt; the excess in the quantity being due to the mercury which must necessarily be liberated during the process of formation of this compound. Now, it is certain that alcoholic mercurous perchlorate will give the β-oxymercuric salt, though impure, when treated with a reducing agent, such as acetaldehyde. At present, the author cannot tell with certainty how far the reduction of the mercurous salt will go in such a case, because he has no sufficient supply of mercury perchlorates to make further experiments, yet it is probable that such a change will always take place to a greater extent, and the use of aldehyde gives promise of satisfactory results in the preparation of the β-salt on a large scale.

6. STABILITY OF AQUEOUS PERCHLORIC ACID.

The remarkable stability of such acid has hitherto been so strongly urged that it is not reduced, as Berthelot[1] states, even with hydrogen sulphide, sulphurous acid, nitrous acid, or by any other reducing agent. These statements may be taken as practically true, but they are not strictly so when examined more exactly. The author has recently been able to prove that the perchloric acid radical acts on alcohol so as to give aldehyde but would never be reduced so far as to hydrochloric acid. He may now add another fact; namely, that hydrogen sulphide is in fact able to reduce the free acid, though in a slight degree. He has already stated[2] that perchloric acid, after the precipitation of mercury with hydrogen sulphide, always becomes contaminated with sulphuric acid upon evaporation. Since it is a matter of common fact that aqueous hydrogen sulphide does not oxidise much even on prolonged evaporation, the formation of sulphuric acid in the above case must be attributed to the oxidising action of the perchloric acid present. Now expecting to ascertain how far such reduction will go, he has made a series of brief experiments as shown in the following:—

[1] Bull. Soc. Chim., [2], **38**, 1.

[2] *Loc. cit.*

(i) 2 c.c. of aqueous perchloric acid containing about 70 per cent. of the acid, obtained by distillation, were mixed with 15 c.c. of a strong solution of hydrogen sulphide. Evaporated until its odour was no longer observed, the solution was found to contain about 0.0007 gr. of *sulphuric acid*, which just corresponds to 0.04 per cent. of perchloric acid reduced from the original solution.

(ii) 20 c.c. of aqueous perchloric acid, containing 4·385 gr. of the acid, were mixed with an excess of the concentrated solution of hydrogen sulphide, and evaporated in the same way as before. The *sulphuric acid* formed was found in one experiment to be 0·0024 gr., which corresponds to 0·06 per cent. of the reduced perchloric acid; and in another 0·0040 gr., corresponding to 0.09 per cent. of the reduced acid.

Admitting the results of these experiments as correct, it may be concluded that the reduction of perchloric acid will proceed to a certain extent under particular conditions. Further experiments with nitrous acid, etc., have, however, not yet been carried out, but will be postponed to some future time when the author expects to take up the studies of the same subject.

Reaction between Silver Nitrate and Disodium Hydrogen Phosphate.

By

Yukichi Osaka.

It is well known that silver phosphate is incompletely precipitated when silver nitrate and disodium hydrogen phosphate are mixed in equivalent proportions. Recently M. Berthelot[1] investigated the reactions which take place when these two salts are mixed in different proportions, and represented them by somewhat complicated equations. It seems, however, as if he did not take into account the influence of dilution on the condition of equilibrium. I have lately undertaken the studies of the reaction for the same substances from the physico-chemical standpoint and found some relations in the equilibrium.

Silver nitrate, of the purest quality obtained from Merk and which was neutral to litmus, was used; the disodium hydrogen phosphate was the ordinary kind thrice recrystallised; and the water, used as the solvent, was distilled with a tin condenser. A calculated amount of each salt was taken and dissolved to a solution of the required concentration in a thermostat at a temperature of $25{\cdot}0^\circ \pm 0{\cdot}1^\circ$ and both solutions were then mixed in a flask in the same bath. The mixture was filtered with due precautions, and the concentration of silver in the solution was determined by a standard solution of potassium thiocyanate by Volhard's method. It was a matter of perfect indifference whether the filtration is performed immediately on mixing, or after twenty-four hours.

1 Compt. rend. **132**, 1449 (1901.)

When the two salts are mixed in equivalent proportions, the following results were obtained:

Table I.

Concentration of silver in the mixed solution.		Concentration of the acidic hydrogen.	Silver precipitated per cent.
Before the reaction.	After the reaction.		
0·0050	0·00241	0·00167	51·8
0·0100	0·00483	0·00333	51·7
0·0150	0·00737	0·00500	50·8
0·0200	0·00940	0·00667	53·0
0·0250	0·0118	0·00833	52·8
0·0300	0·0141	0·01000	53·0
0·0400	0·0186	0·0133	53·5
0·0500	0·0227	0·0167	54·6
0·0600	0·0268	0.0200	55·4
0·0700	0·0306	0·0233	56·3
0·0800	0·0348	0·0267	56·5
0·0900	0·0386	0·0300	57·1
0·1050	0·0437	0·0350	58·1
0·1200	0·0492	0·0400	59·0

The concentrations, as represented in the table, are expressed in mols (or gram-radicals) per litre. As will be seen from the table, the percentage amount of the precipitated silver increases with concentration,[1] but the increment of the percentage amount of the precipitate is comparatively small.

The solubility of silver phosphate in dilute nitric acid of different concentration, was next determined. Silver phosphate was precipitated by the addition of an excess of disodium hydrogen phosphate to a solution of silver nitrate: the precipitate being

[1] Excluding a few cases of solutions of comparatively high dilution, in which the experimental errors have a considerable influence on the results.

well washed with water and dried on a porous tile. A portion of it was further dried over sulphuric acid and analysed: it contained 77·0 per cent. of silver; while the theoretical amount for PO_4Ag_3 is 77·2. In determining its solubility, silver phosphate thus prepared was twice washed by shaking it with a portion of the dilute nitric acid in which its solubility was to be determined; and by this means some admixtures, which might have been present, would have been washed away. The results are as follows:

Table II.

Concentration of nitric acid.	Concentration of silver in the solution.
0·0050	0·00748
0·0100	0·0142
0·0150	0·0206
0·0200	0·0263
0·0250	0·0325
0·0300	0·0387
0·0350	0·0434
0·0400	0·0494

If we compare the tables, I and II, it will be seen that when the concentration of the acidic hydrogen in table I, is equal to the concentration of the nitric acid in table II, the concentration of silver in the solutions is the same in both cases.

This relation may easily be explained: the reaction between silver nitrate and disodium hydrogen phosphate may be represented by the equation:

$$3NO_3Ag + PO_4HNa_2 = PO_4Ag_3 + NO_3H + 2NO_3Na,$$

and when the solutions are dilute, the electrolytic dissociation of the metallic salts and of the nitric acid may be regarded as practically complete. Therefore, the equation may be transformed as follows:

$$3Ag^{\cdot} + PO_4H'' \rightleftharpoons PO_4Ag_3 + H^{\cdot}:$$

and this is also the equation which represents the reaction

between silver phosphate and nitric acid. It must be remarked, however, that the equation does not represent the reaction fully; for it is evident that the following reactions also take place in the solution:

$$PO_4H'' + H^{\cdot} \rightleftharpoons PO_4H_2',$$
$$PO_4H_2' + H^{\cdot} \rightleftharpoons PO_4H_3.$$

Since the presence of sodium nitrate has no remarkable influence upon the equilibrium, as we have seen, we shall take the results in tables I and II together, and consider theoretically the conditions of the equilibrium of the reaction in question.

Phosphoric acid is tribasic and not very weak; and these facts bring forth many difficulties in finding a simple theoretical relation in the equilibrium which may be verified by the results of observation. Only under certain assumptions a simple relation has been deduced as follows: in the solutions investigated, the total concentration of silver was always greater than the concentration of the nitric acid radical, and since nitric acid is much stronger than phosphoric acid, it will be assumed that in practice nitric acid is completely neutralised by silver and that the rest of the silver neutralises a portion of the phosphoric acid. If, under this assumption, we calculate the ratio of the free and neutralised parts of the phosphoric acid, it will be found to vary between 2 : 1 and 4 : 1, in the limits of the concentrations now investigated. Thus, we may assume that the solutions contain principally siver nitrate, silver dihydrogen phosphate, and free phosphoric acid, together with their dissociation products.

Let C_1 represent the total concentration of the free phosphoric acid, and C_2 that of its monosilver salt; and let the concentration of the different molecules and ions be represented by enclosing their respective formula in brackets, as for example, $[PO_4H_3]$, $[H^{\cdot}]$, $[Ag^{\cdot}]$, etc. Since it is assumed that the electrolytic dissociation of the metallic salts is practically complete, the concentration of the ion PO_4H_2' from PO_4H_2Ag is also C_2, and as we may assume that the electrolytic dissociation of phosphoric

acid is practically binary,[1] if K_1 denote the dissociation constant of phosphoric acid and γ the degree of its electrolytic dissociation, we have the following relations:

$$[PO_4H_3]=(1-\gamma)C_1,$$
$$[PO_4H_2']=\gamma C_1+C_2,$$
$$[H^{\cdot}]=\gamma C_1,$$

and for the electrolytic dissociation of phosphoric acid we have:

$$K_1(1-\gamma)C_1=(C_2+\gamma C_1)\gamma C_1.$$

Hence:

$$\gamma C_1=\frac{\sqrt{(C_2+K_1)^2+4K_1C_1}-(C_2+K_1)}{2}$$

As stated above, the electrolytic dissociation of phosphoric acid may be regarded practically as binary, but it proceeds further, though only in a slight degree, and the solutions contain also a very small amount of the ion PO_4'''. Let K_2 and K_3 represent the dissociation constants of phosphoric acid with regard to the second and third hydrogen respectively, then we have:

$$K_2[PO_4H_2']=[PO_4H'']\,[H^{\cdot}],$$

and

$$K_3[PO_4H'']=[PO_4'''][H^{\cdot}].$$

Therefore;

$$[PO_4'''']=K_2K_3\frac{[PO_4H_2']}{[H^{\cdot}]^2}=K_2K_3\frac{C_2+\gamma C_1}{(\gamma C_1)^2}.$$

Since the solutions are saturated with silver phosphate, we have:

$$[PO_4'''']\,[Ag^{\cdot}]^3=\text{const.}^2$$

and consequently:

$$\frac{C_2+\gamma C_1}{(\gamma C_1)^2}[Ag^{\cdot}]^3=\text{const.}$$

In order to verify this relation by the results of observation, it is necessary to know the value of K_1. O.E.Tower[3] has calculated it from the conductivity of its solutions at $15°C.$, and

[1] *Cf.* Jones, Zeitschr. f. physik. Chem. **12**, 630 (1893).

[2] According to Böttger, the solubility product of silver phosphate at 19·46° is $1{\cdot}39{\cdot}10^{-18}$ (Zeitschr. f. physik. Chem., **46**, 566, 1903).

[3] Zeitschr. f. physik. Chem. **18**, 32, (1895).

found it to vary gradually from 0·0101 to 0·0071, when the dilution increases from 12·5 to 6400. As noticed because of its heat of neutralisation, the electrolytic dissociation of phosphoric acid will diminish as the temperature rises, and although it is rather arbitrary, the assumption will be made here that the dissociation constant of phosphoric acid at 25° is 0·007.

Let A denote the concentration of the acidic hydrogen in the solutions and S that of the silver. Since the concentration of the nitric acid radical is also A (of course excluding sodium nitrate in the case, if any is present), that of the silver which neutralises phosphoric acid is $S-A$, and therefore we have:

$$C_2=S-A,$$

and

$$C_1=\frac{A-2C_2}{3}=\frac{3A-2S}{3}.$$

As will be seen from the table given below, the difference of two magnitudes which do not differ much from each other, comes into play in these expressions, and the errors of observation will exert a considerable influence upon the results. Excluding the cases of comparatively great dilution, the following table has been calculated:

Table III.

S.	A.	$S-A=C_2$.	$\frac{3A-2S}{3}=C_1$.	γC_1.	$\frac{C_2+\gamma C_1}{(\gamma C_1)^2}S^2$.
0·0186	0·0133	0·0053	0·0093	0·0005	0·15
0·0206	0·0150	0·0056	0·0013	0·0007	0·11
0·0227	0 0167	0·0060	0·0015	0·0008	0·12
0·0266	0·0200	0·0066	0·0023	0·0011	0·12
0·0306	0·0233	0·0073	0·0029	0·0013	0·15
0·0325	0·0250	0·0075	0·0033	0·0014	0·16
0·0348	0·0267	0·0081	0·0035	0·0015	0·18
0·0386	0·0300	0·0086	0·0043	0·0016	0·23
0 0436	0·0350	0·0086	0·0059	0·0023	0·22
0·0493	0·0400	0·0093	0·0071	0·0027	0·20

The magnitudes in the last column are not satisfactory, but it will perhaps be impossible to expect any better results than those, because in addition to the inexactness of the dissociation constant of phosphoric acid adopted in the present case, certain approximation has been made in deriving the final expression and moreover the errors of observation exert a considerable influence upon the results of the calculation.

When an excess of silver nitrate was added to a solution of disodium hydrogen phosphate, the following results were obtained:

Table IV.

Concentration of the salts in the mixed solution before the reaction.		Concentration of silver in the solution after the reaction.
Disod. hydrogen phosphate.	Silver nitrate.	
	(1)	
0·0050	0·0150	0·0073
„	0·0300	0·0217 = „ + 0·0144
„	0·0450	0·0360 = „ +2× „ −0·0001
„	0·0600	0·0506 = „ +3× „ +0·0001
„	0·0750	0·0648 = „ +4× „ −0·0001
	(2)	
0·0100	0·0300	0·0139
„	0·0600	0·0418 = „ + 0·0280 −0·0001
„	0·0900	0·0700 = „ +2× „ +0 0001
„	0·1200	0·0975 = „ +3× „ −0·0004
„	0·1500	0·1261 = „ +4× „ +0·0002

As will be seen, when the number of equivalents of silver nitrate, which is added to one equivalent of disodium hydrogen phosphate, is increased, the increment of the precipitate is very slight and proportional, within the limits of the experimental errors, to the number of equivalents added in excess.

Under the same assumptions as already stated, we shall consider the results from the theoretical standpoint. Even when

silver nitrate was used in excess, as long as the total concentration of the metallic radicals is greater than that of the nitric acid radical, the condition of the equilibrium may be represented by the same expression as that derived for the mixture of equivalent proportions. Let S_0 denote the concentration of the silver nitrate taken; and if S, A, C_1 and C_2 have the same significance as before, we deduce from table IV the following one:

Table V.

S_0.	S.	A.	$S-(S_0-2A)-C_2$.	$\frac{3A-(S_0-S)}{3}-C_2-C_1$.	γC_1.	$\frac{C_2+\gamma C_1}{(\gamma C_1)^2}S^3$
0·0300	0·0217	0·0050	0·0017	0·0005	0·0004	0·13
0·0450	0·0360	0·0050	0·0010	0·0010	0·0008	0·13
0·0600	0·0506	0·0050	0·0006	0·0012	0·0010	0·21
0·0600	0·0418	0·0100	0·0018	0·0021	0·0012	0·15

When the total concentration of the metallic radicals is smaller than that of the nitric acid radical, let C_3 denote the concentration of the free nitric acid, then we have:

$$[H^{\cdot}]=\gamma C_1+C_3,$$

and for the electrolytic dissociation of phosphoric acid we have:

$$K_1(1-\gamma)C_1=\gamma C_1(\gamma C_1+C_3),$$

and therefore:

$$\gamma C_1=\frac{\sqrt{(\gamma C_1+C_3)^2+4KC_1}-(C_3+K)}{2}.$$

Since:

$$[PO_4'''']=K_1K_2K_3\frac{[PO_4H_3]}{[H^{\cdot}]^3},$$

for the solubility product of silver phosphate we have:

$$K_1K_2K_3\frac{\gamma C_1}{(\gamma C_1+C_3)^3}S^3,$$

and for the expression, which should give the same constant as before, we have:

$$0{\cdot}007\frac{\gamma C_1}{(\gamma C_1+C_2)^3}S^2=\text{const.}$$

For the verification of the last equation, the following table has been calculated:

Table VI.

S_0	$S.$	$A.$	S_0-2A-S $-C_2$	$A-\frac{S_0-S}{3}$ $-C_1.$	γC_1	$0.007\frac{\gamma C_1}{(\gamma C_1+C_2)^3}S^2$
0·1200	0·0975	0·0100	0·0025	0·0025	0·0016	0·15
0·1500	0·1261	0·0100	0·0039	0·0020	0·0012	0·13

Thus, the constants in the tables, V and VI, are pretty nearly concordant with those in table III, and although rather too much approximation has been permitted in the calculations, it is highly probable that the agreement between the theoretical and experimental results, is not mere accident.

When disodium hydrogen phosphate was used in excess, the following results were obtained:

Table VII.

Concentration of the salts in the mixed solution before the reaction		Concentration of silver in the solution after the reaction	Silver precipitated per cent.
Disod. hydrogen phosphate.	Silver nitrate.		
	(1)		
0.0100	0·0300	0·0138	54
0·0200	"	0·00056	98
0·0300	"	0·00012	100
	(2)		
0·0200	0·0600	0·0271	55
0·0300	"	0·0136	77
0·0400	"	0·00074	99
0·0500	"	0·00011	100

Thus, the influence of an excess of the phosphate is very great, and this fact may be explained in the following way: In this case, while the concentration of the nitric acid radical remains constant, the amount of disodium hydrogen phosphate increases and the concentration of the hydrogen ions diminishes because of the following reaction:

$$PO_4H'' + H^{\cdot} = PO_4H_2'$$

Consequently the concentration of the ion PO_4''' increases very rapidly, when the amount of disodium hydrogen phosphate is increased, and somewhat less so than three equivalents of disodium hydrogen phosphate to one of silver nitrate is sufficient practically to precipitate completely the silver as the phosphate.[1]

SUMMARY.

1. When silver nitrate and disodium hydrogen phosphate are mixed in equivalent proportions, the percentage amount of the precipitate increases with the concentration, but the rate of the increment is comparatively small.

2. When the two salts are mixed in equivalent proportions, the concentration of the silver remaining in the solution is the same as that of the saturated solution of silver phosphate in dilute nitric acid, of which the concentration is equal to the concentration of the acidic hydrogen in the former.

3. The influence of an excess of silver nitrate in increasing the precipitate is slight, and a simple relation has been found between the amount of silver nitrate used in excess and that of the precipitate.

4. An excess of disodium hydrogen phosphate has a considerable influence in increasing the amount of the precipitate.

5. The conditions of the equilibrium of the reaction have been theoretically discussed and verified by the experiments.

[1] *Cf.* Berthelot, *l. c.*

April, 1905.

Note on the Action of Phosphorus Pentachloride upon Tartranil.

By

Sadajiro Okada.

At the suggestion of Prof. Kuhara, the author has undertaken to study the action of phosphorus pentachloride upon dextro-tartranil,

$$C_2H_2(HO)_2\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle N\cdot C_6H_5,$$

prepared from dextrotartaric acid and aniline, and has observed that the chlorination takes place, in two ways at the same time, in such a manner as to produce dichlormaleinanil,

$$\begin{matrix}CCl-CO\\ \|\\ CCl-CO\end{matrix}\Big\rangle N\cdot C_6H_5,$$

on the one hand, and n-phenyltetrachlorpyrrol,

$$\begin{matrix}CCl=CCl\\ |\\ CCl=CCl\end{matrix}\Big\rangle N\cdot C_6H_5$$

on the other: the latter could readily have been transformed into n-phenylpyrrol. The reactions involved in the chlorination, then, should be as follows:

$$\text{I,}\quad \begin{matrix}CH\cdot OH-CO\\ |\\ CH\cdot OH-CO\end{matrix}\Big\rangle N\cdot C_6H_5+3PCl_5$$

$$=\begin{matrix}CCl-CO\\ \|\\ CCl-CO\end{matrix}\Big\rangle N\cdot C_6H_5+2POCl_3+PCl_3+4HCl.$$

II,a. $$\begin{array}{l} CH{\cdot}OH-CO \\ | \\ CH{\cdot}OH-CO \end{array}\!\!>N{\cdot}C_6H_5 + 4PCl_5$$

$$= \begin{array}{l} CHCl-CCl_2 \\ | \\ CHCl-CCl_2 \end{array}\!\!>N{\cdot}C_6H_5 + 4POCl_3 + 2HCl,$$

II,b. $$\begin{array}{l} CHCl-CCl_2 \\ | \\ CHCl-CCl_2 \end{array}\!\!>N{\cdot}C_6H_5 = \begin{array}{l} CCl=CCl \\ | \\ CCl=CCl \end{array}\!\!>N{\cdot}C_6H_5.$$

The fact that in reaction I. dichlormaleinanil is formed instead of dichlorsuccinanil being produced, may readily be explained upon the assumption that the dichlorsuccinanil, which is first produced from dextrotartranil, will immediately be transformed into monochlormaleinanil, owing to its most favorable configuration for giving up a molecule of hydrochloric acid: but the monochloramaleinanil so formed may scon replace its hydrogen with chlorine, producing dichlormaleinanil, as will be seen from the following scheme of transformation:

$$\begin{array}{l} CO \\ | \\ H-C-OH \\ | \\ HO-C-H \\ | \\ CO \end{array}\!\!>N{\cdot}C_6H_5 \xrightarrow{+2PCl_5} \begin{array}{l} CO \\ | \\ H-C-Cl \\ | \\ Cl-C-H \\ | \\ CO \end{array}\!\!>N{\cdot}C_6N_5 \xrightarrow{-HCl}$$

$$\rightarrow \begin{array}{l} CO \\ | \\ H-C \\ \| \\ Cl-C \\ | \\ CO \end{array}\!\!>N{\cdot}C_6H_5 \xrightarrow{+Cl_2} \begin{array}{l} CO \\ | \\ Cl-C \\ \| \\ Cl-C \\ | \\ CO \end{array}\!\!>N{\cdot}C_6H_5$$

EXPERIMENTALS.

On treating the dextrotartranil prepared from dextrotartaric acid and aniline, according to the directions of Arrpe,[1] with phosphorus pentachloride at ordinary, or slightly elevated temperature, a reddish brown liquid was produced. The phosphorus compounds were then distilled off under diminished pressure and a solution obtained by treating the residue with petroleum ether, deposited brown coloured, fine crystals. By repeated recrystallisation from hot alcohol, crystals were finally obtained in the form of white plates with silky lustre. The melting point of this substance was found to be 202°–204°, and it was capable of sublimation. It was soluble in alcohol, acetic acid, ether, and petroleum ether, but with difficulty in water. It was analysed and the following results were obtained:

	Calculated for $C_{10}H_5Cl_2NO_2$.	Found. I.	II.	III.
Carbon	49·59	49·39	.....	.....
Hydrogen	2·87	2·91	.....	.....
Nitrogen	5·80	.....	5·82	.....
Chlorine	29·30	.....	.....	29·49

The analysis, as well as the physical and chemical properties of the substance, show that it is identical with the dichlormaleinanil obtained by Kauder[2] from succinanil by phosphorus pentachloride.

By spontaneous evaporation of the mother liquor (petroleum ether solution) from dichlormaleinanil, beautiful, large, well-defined crystals were deposited. They were observed to have all the preperties of n–phenyltetrachlorpyrrol prepared by Anschütz and Beavis[3] from succinanil by phosphorus pentachloride. On treating the alcoholic solution of n–phenyltetrachlorpyrrol with sodium amalgam, white, scaly crystals, with pearly lustre

[1] Ann. d. Chem., **93**, 352.
[2] J. prakt. Chem., [2], **31**, 17.
[3] Ann. d. Chem., **295**, 30.

were deposited. They have the properties identical with those of n–phenylpyrrol obtained by Köttnitz[1] from aniline mucilate, as well as that obtained by Lichtenstein[2] from aniline saccharate, by dry distillation in each case. The substance was analysed, and its nitrogen determined, as follows :

	Calculated for $C_{10}H_9N$.	Found. I.	Found. II.
Nitrogen	9·81	9·43	9·83

[1] J. prakt. Chem., [2], **6**, 148.
[2] Ber. d. chem. Ges., **14**, 933.

December, 1904.

明治三十八年七月十五日印刷
明治三十八年七月二十日發行

編纂兼發行者　京都帝國大學理工科大學

印刷者　東京市京橋區築地三丁目十五番地
野村宗十郎

印刷所　東京市京橋區築地二丁目十七番地
株式會社東京築地活版製造所

CONTENTS.

On the Distribution of Iodine between Two Solvents. PAGE.
By Yukichi Osaka 93

On the Equilibrium of the Electrolytic Dissociation of Partially Neutralised Acids and Bases.
By Yukichi Osaka 103

Action of Ammonia and of Amines upon Chloral.
By Mitsuru Kuhara and Yoshinori Kishi 114

Occurrence of Cerasite and Chiastolite in a Metamorphosed Clay Slate.
By Tadasu Hiki. 125

Retardation Tests with an Unloaded, Covered Railway Wagon.
By Sakurō Tanabe 137

On the Electromagnetic Screening Effect of Metallic Conductors.
By Kunito Ogawa 140

Action of Alcohol upon Mercury Perchlorates.
By Masumi Chikashige 145

Reaction between Silver Nitrate and Disodium Hydrogen Phosphate.
By Yukichi Osaka 158

Note on the Action of Phosphorus Pentachloride upon Tartranil.
By Sadajiro Okada 1

OCT 12 1907
CAMBRIDGE, MASS.

Oct 12, 5. 7
Box ash)

The College

MEMOIRS

OF THE

COLLEGE OF SCIENCE AND ENGINEERING,

KYŌTO IMPERIAL UNIVERSITY.

VOL. I., No. 3.

1906—1907.

KYŌTO.

1907.

PUBLICATION COMMITTEE:

Professor	MITSURU KUHARA
Do.	HAN-ICHI MURAOKA
Do.	MASASHI NAMBA
Do.	SAKURŌ TANABE
Do.	TOSHINOJŌ MIZUNO.

These Memoirs contain original articles by the members of the University. They are not intended to be published at regular intervals. Each volume will be separated into 6 numbers of about 100 pages each.

Equilibrium between Reciprocal Salt-Pairs.

By

Yukichi Osaka and **Jingoro Yamasaki.**

ERRATA.

Page	212,	line	10	from top,	read	"8, 9,.....,"	for	"8,.....,"
„	217,	„	6	„ bottom,	„	"$\pi L\sqrt{\frac{\rho \text{ arc } 1'}{12\, I s}}$"	„	"$L\sqrt{\frac{\rho \text{ arc } 1'}{12\, I s}}$"
„	218,	„	10	„ top,	„	"3·53"	„	"4·26"
„	222,	„	9	„ bottom,	„	"0·95"	„	"1·15"
„	„	„	„	„	„	"3·53"	„	"4·26"

deviation to the fact that Morgan neglected [illegible] composition of those sparingly soluble barium salts which will not be a trifle in such high dilution. Similarly, in the case of strontium salts, the equivalent ratio of the sulphate and carbonate has been calculated to be 60 : 1, under the assumption that no hydrolitic decomposition takes place.[1]

So far as we know, any quantitative experimental work on the equilibrium of the latter case is not found in the literature and hence it seems to us that to determine experimentally the condition of the equilibrium of the reaction, will not be without interest. While our experiments were in progress, there appeared an elaborate

[1] The treatise by Morgan (Journ. Amer. Chem. Soc. **21**, 522, 1899) and that by Küster (Verh. d. Vers. Deutsch. Ntf. u. Ärzte, 1899) were not accessible to us, and the citations here made are taken from an abstract of the latter in Chem. Centralbl. **71**^{II}, 544.

PUBLICATION COMMITTEE:

Professor	MITSURU KUHARA
Do.	HAN-ICHI MURAOKA
Do.	MASASHI NAMBA
Do.	SAKURŌ TANABE
Do.	TOSHINOJŌ MIZUNO.

These Memoirs contain original articles by the members of the University. They are not intended to be published at regular intervals. Each volume will be separated into 6 numbers of about 100 pages each.

Equilibrium between Reciprocal Salt-Pairs.

By

Yukichi Osaka and **Jingoro Yamasaki.**

According to the classical work of Guldberg and Waage upon the equilibrium between the reciprocal salt-pairs:

$$SO_4Ba + CO_3K_2 \rightleftharpoons CO_3Ba + SO_4K_2$$

the sulphate and carbonate in the solution are in the ratio of 1 equivalent to 4, when equilibrium is established at 100°C. Morgan has lately calculated such relationship by means of the solubility products of barium sulphate and carbonate, and has reached the conclusion that it is 1 : 105, in a vast deviation with the experimental results referred to above. Küster has ascribed such a deviation to the fact that Morgan neglected the hydrolytic decomposition of those sparingly soluble barium salts which will not be a trifle in such high dilution. Similarly, in the case of strontium salts, the equivalent ratio of the sulphate and carbonate has been calculated to be 60 : 1, under the assumption that no hydrolitic decomposition takes place.[1]

So far as we know, any quantitative experimental work on the equilibrium of the latter case is not found in the literature and hence it seems to us that to determine experimentally the condition of the equilibrium of the reaction, will not be without interest. While our experiments were in progress, there appeared an elaborate

[1] The treatise by Morgan (Journ. Amer. Chem. Soc. **21**, 522, 1899) and that by Küster (Verh. d. Vers. Deutsch. Ntf. u. Ärzte, 1899) were not accessible to us, and the citations here made are taken from an abstract of the latter in Chem. Centralbl. **71**^{II}, 544.

work of Meyerhoffer[1] on the barium salts; and, among others, it was shown that the ratio, 1 : 4, found by Guldberg and Waage, is not constant, but varies with the total concentration of the potassium salts, as well as with the temperature. We were, therefore, desirous of working with the various concentrations of the potassium salts; but, under certain circumstances, we have confined ourselves to a single total concentration of 0·5 normal.

The experiments were carried out in the manner described as follows: certain quantities of strontium carbonate and sulphate, both prepared by precipitation and dried at about 110°, were put into an Erlemmeyer flask made of silver, having a capacity of 300 c.c.; about 200 c.c. of a mixed solution of potassium sulphate and carbonate of the total concentration of 0·5 normal were added, and the contents were boiled for 24 hours with a reverse condenser of silver. Then the solution was filtered quickly while hot and, when cool, 50 c.c. of the contents were taken out and titrated with a standard solution of hydrochloric acid of about n/50, using methyl orange as an indicator. The sulphate was determined as barium sulphate in the usual way. If the experiments had been conducted with an unmixed solution of the sulphate or carbonate, a considerable period of time must have elapsed before the equilibrium was attained. In the preliminary experiments, therefore, the equilibrium point was approximately determined, and the solutions were used which deviated somewhat in composition from those in equilibrium. The results obtained were as follows:

Table I.

Initial solution.		Final solution.		
Sulphate (g. equivalent per litre.)	Carbonate (g. equivalent per litre.)	Sulphate (g. equivalent per litre.)	Carbonate (g. equivalent per litre.)	Sulphate / Carbonate
0·493	0·007	0·5046	0·00534	94·6
,,	,,	0 5077	0·00513	98·9

[1] Zeitschr. f. physik. Chem. **53**, 513 (1905).

0·493	0·007	0·5085	0·00529	96·1
0·494	0·006	0·5098	0·00535	95·3
,,	,,	0·5337 (?)	0·00527	—
0·4945	0·0055	0·4999	0·00534	93·7
,,	,,	0·5051	0·00535	94·4
,,	,,	0·5109	0·00535	95·5
,,	,,	0·5058	0·00533	94·9
0·49452	0·00548	0·5139	0·00535	96·0
,,	,,	0·5103	0·00532	95·9
			Mean	95·5

Table II.

Initial solution.		Final solution.		
Sulphate (g. equivalent per litre.)	Carbonate (g. equivalent per litre.)	Sulphate (g. equivalent per litre.)	Carbonate (g. equivalent per litre.)	Sulphate / Carbonate
0·495	0·005	0·5017	0·00543	92·4
,,	,,	0·5134	0·00524	98·0
,,	,,	0·5090	0·00523	97·3
0·4948	0·0052	0·5051	0·00531	95·1
,,	,,	0·5009	0·00532	94·1
0·4947	0·0053	0·5050	0·00531	95·1
,,	,,	0·5046	0·00536	94·1
,,	,,	3·5098	0·00534	95·5
0·49469	0·00531	0·5098	0·00533	95·6
,,	,,	0·4993	0·00529	94·4
,,	,,	0·4976	0·00530	93·9
			Mean	95·0

The increase in the total concentration of the solution, observed after the experiment, is evidently due to some loss of water during the long boiling of the solution.

In conclusion we may say that, in a solution of potassium sulphate and carbonate of the total concentration of 0·5 normal which are in equilibrium with strontium sulphate and carbonate at 100° C., the sulphate and carbonate are in equivalent ratio of 95 : 1 approximately.

Reaction between Carbonic Acid and Lead Acetate in an Aqueous Solution.

By

Jingoro Yamasaki.

Walchnel[1] has ever shown that the precipitation of lead carbonate is incomplete when carbonic acid gas is passed through an aqueous solution of lead acetate. Gustav Bischof[2] has studied the same reaction, and from some observations made by him, he has drawn the conclusion that the amount of lead carbonate precipitated from a given quantity of lead acetate is, approximately, proportional to the initial dilution of the lead salt, and that, when the solution is so dilute that water is more than thirteen times as much as the amount of the salt, the precipitation is almost independent of dilution. The author has undertaken the study of the same reaction in greater detail; the present paper being a résumè of the chief results thus far obtained.

Commercial lead acetate was twice recrystallised from its solution acidified with acetic acid, and dried by pressing between filter papers. It gave a white precipitate with potassium ferrocyanide, and by an analysis its composition, $(CH_3CO_2)_2Pb.3H_2O$, was confirmed as being what was to have been expected.

Carbon dioxide was generated in a Kipp's apparatus with marble and hydrochloric acid, washed with a saturated solution of sodium bicarbonate, and then passed through an U-tube filled with cotton wool.

The experiments were carried out as follows:—Three Erlen-

[1] Schweigger's u. Schweigger Seidel's Journ. **48**, 257.
[2] Journ. f. prakt. Chem. **7**, 181.

meyer flasks of about 100 c.c. capacity, each charged with about 30 c.c. of the solution, were connected in a series, in such a manner as to allow the passage of carbon dioxide through them successively. They were then immersed in a thermostat of 25°C. The solutions were saturated with carbon dioxide and filtered with every possible precaution. 20 c.c. of each solution were taken out with a pipette, and the lead was precipitated by the addition of an excess of potassium sulphate: it was diluted with water and boiled in a reverse condenser in order to expel the dissolved carbon dioxide, and, when cooled, the quantity of free acetic acid present was determined by titration with a decinormal solution of sodium hydroxide, prepared from metallic sodium, using phenolphthalein as an indicator. As the analytical results for the solutions from the three flasks all agreed well, it was evident that the solutions had been saturated with carbon dioxide. Since lead oxide and acetic acid are weak as a base and as an acid, respectively, the author was obliged to use the analytical method above mentioned, which was verified as follows:

(1) 10 c.c. of an acetic acid solution were titrated, using phenolphthalein as an indicator, with a decinormal sodium hydroxide solution, of which the following amounts were needed:

(1)	(2)	Mean.
20·75	20·75	20·75

(2) Carbon dioxide was passed through another portion of the same acetic acid solution in three Erlenmeyer flasks (marked a, b, c.) for three hours. 10 c.c. of the solution were taken out from each flask, and the acetic acid present was determined in a manner similar to that already described, but without the addition of potassium sulphate. The quantities of the decinormal sodium hydroxide needed were:

(1)	(2)	(3)	Mean.
20·75	20·71	20·74	20·73

(3) The process was the same as in the last; the only difference being the addition of 10 c.c. of a normal solution of

potassium sulphate before the boiling of the solution. The results were as follows:

(a)	(b)	(c)	Mean.
20·72	20·74	20·75	20·74

On conducting the experiments by passing carbon dioxide through the solution of lead acetate of various concentrations, the results thus far obtained are stated below:

Table I.

Initial equivalent concentration of lead acetate.	n/10 sodium hydroxide needed for the neutralisation of the free acetic acid in 20 c.c. of the solution, after the reaction.			
	(a)	(b)	(c)	Mean.
2·0	201·0	201·05	201·0	201·0
1·0	111·6	111·9	—	111·7
0·4	—	56·8	56·7	56·8
0·2	30·40	30·50	30·40	30·43
0·1	16·25	16·20	16·23	16·23
0·0667	10·68	10·70	—	10·69
0·0500	8·20	8·23	8·20	8·21
0·0400	6·40	6·39	6·40	6·40
0·0333	5·35	5·45	5·30	5·37
0·0286	4·62	4·65	4·60	4·62
0·0250	4·15	4·10	4·10	4·12
0·0222	3·65	3·60	3·60	3·62
0·0200	3·20	3·23	—	3·21

From the data given above, the following table was obtained by calculation:

Table II.

Before the reaction.	After the reaction.		
Lead acetate.	Acetic acid.	Lead acetate.	$\frac{\text{Acetic acid}}{\text{Lead acetate}}$
2·0	1·0050	0·995	1·01
1·0	0·5590	0·441	1·31
0·4	0·2838	0·1162	2·40
0·2	0·1517	0·0483	
,,	,,	0·0485*	3·14
0·1	0·0812	0·0188	4·32
0·0667	0·0535	0·0132	4·05
0·0500	0·0410	0·0090	4·55
0·0400	0·0324	0·0076	
,,	,,	0·0079*	4·10
0·0333	0·0267	0·0064	4·20
0·0286	0·0231	0·0055	4·20
0·0250	0·0206	0·0044	
,,	,,	0·0040*	4·70
0·0222	0·0181	0·0041	4·41
0·0200	0·0161	0·0039	4·13

In the last table, the equivalent concentrations of lead acetate, after reaction, were calculated from its initial concentration and that of the free acetic acid, except those marked *; and the latter were determined direct, by precipitating lead as sulphate: the results in both cases show, as will be seen, almost complete agreement. As is indicated by the table, the simple relation observed by Bischof—namely, that the quantity of the precipitate in the comparatively concentrated solutions, is approximately proportional to the initial concentration of the lead acetate, is not true. Moreover, he has found that when the quantity of water is more than thirteen times the amount of lead acetate, the precipitate is independent of the initial dilution. According to the present experiments, however, it is constant when the concentration is not higher than 0·1 normal, or if the quantity of water is more than fifty times that of the acetate. The author

wonders, therefore, if Bischof worked at ordinary temperatures, as the deviation is somewhat too great to be ascribed to a small difference in the temperatures at which the experiments were conducted. With regard to the influence of temperature in the reaction of the present problem, its consideration will be deferred till the future.

Now, the chemical reaction, so far, may be represented as reversible :

$$(CH_3CO_2)_2Pb + CO_3H_2 \rightleftharpoons 2CH_3CO_2H + CO_3Pb$$

and it is evident that, if the concentration of the acetic acid be increased, the amount of the precipitate will decrease, as will be confirmed by the experiment hereinafter to be described.

Table III.

Initial equivalent concentration.		n/10 sodium hydroxide needed for the neutralisation of the free acetic acid in 20 c.c. of the solution after reaction.			
Lead acetate.	Acetic acid.	(a)	(b)	(c)	Mean.
0·0500	0·0500	16·10	16·10	16·05	16·10
0·0250	0·0500	12·00	11·95	12·05	12·00
0·0250	0·0125	6·20	6·15	—	6·17
0·0125	0·0250	5·95	6·00	5·95	5·97
0·0250	0·0250	7·85	7·90	7·90	7·88

From the above data, the following table was deduced by calculation :

Table IV.

Before the reaction.		After the reaction.		
Lead acetate.	Acetic acid.	Acetic acid.	Lead acetate.	$\frac{\text{Acetic acid}}{\text{Lead acetate}}$
0·0500	0·0500	0·0805	0·0195	4·3
0·0250	0·0500	0·0600	0·0150	4·0
0·0250	0·0125	0·0309	0·0072	4·4
0·0125	0·0250	0·0299	0·0070	4·3
0·0250	0·0250	0·0394	0·0100	4·0

As the table shows, when the total concentration of the acetic acid radical is less than 0·1 normal, the addition of acetic acid exerts no remarkable influence upon the proportion of the free acid and the lead salt in the solution after reaction: this is what was to have been expected after the results already obtained.

As to the reaction now under consideration, the influence of acetic acid on the amount of the precipitate may possibly be due to its hydrogen ions: it is, therefore, to be expected that the addition of sodium acetate to the solution would increase the amount of the precipitate. In an experiment for the verification of this view, a solution of sodium acetate was prepared by neutralising acetic acid with sodium hydroxide, obtained from metallic sodium, and various quantities of the solution were added to the lead acetate solution before the passing of carbon dioxide gas. In each experiment, the precipitate was confirmed by analysis as being the normal carbonate. The experimental results were as follows:

Table V.

Initial solution.		n/10 sodium hydroxide needed by the neutralisation of the free acetic acid in 20 c.c. of the solution after the reaction.			
Lead acetate.	Sodium acetate.	(a)	(b)	(c)	Mean.
0·0500	0·0500	9·60	9·65	9·75	9·66
0·0500	0·0250	9·40	9·40	9·30	9·37
0·0400	0·0500	7·85	7·83	—	7·84
0·0250	0·0250	4·98	4·95	5·00	4·98
0·0250	0·0125	4·80	4·85	4·85	4·83
0·0200	0·0250	4·00	4·00	4·00	4·00

From the data given in the above table, the concentration of acetic acid and lead acetate, after the reaction, were calculated, with the results given in the following table:

Table VI.

Before the reaction.		After the reaction.	
Lead acetate.	Sodium acetate.	Lead acetate.	Acetic acid.
0·0500	0·0500	0·0007	0·0483
0·0500	0·0250	0·0031	0·0469
0·0400	0·0500	0·0008	0·0392
0·0250	0·0250	0·0001	0·0249
0·0250	0·0125	0·0008	0·0242
0·0200	0·0250	—	0·0200

Thus, in a dilute solution of lead acetate, when sodium acetate is added in quantity greater than equivalent to the lead salt, the lead may be almost completely precipitated by carbon dioxide, as its normal carbonate.

SUMMARY.

1. The precipitate produced by carbonic acid in a solution of lead acetate, with or without the addition of sodium acetate, is the normal carbonate of lead.

2. The amount of the precipitate from a given quantity of lead acetate, increases with the dilution of the solution; but when the concentration is lower than 0·1 normal, it is independent of dilution.

3. When acetic acid is added to the lead acetate solution, the proportion of the free acid and lead acetate in the solution, after reaction, will be the same as in the case when no acid is previously added, if the total concentration of the acetic acid radical is lower than 0·1 normal.

4. In a dilute solution of lead acetate, the lead may be almost completely precipitated by carbonic acid when sodium acetate is added in quantity more than equivalent to the lead salt.

Versuche zur Nutzbarmachung von Metallabfällen.

Von

Tosio Watanabe.

Beim Ausdrehen von Armaturen und Lagerteilen, welche aus einem Bronzekörper mit Auskleidung von Weißmetall bestehen, fallen Drehspäne, in denen die beiden Metallegierungen in einer Mischung enthalten sind, welche einer rein mechanischen Trennung mancherlei Schwierigkeiten entgegensetzt. Bis zu einem gewissen Grade lassen sich dieselben, da der Schmelzpunkt der sog. weißen Späne ein erheblich niedrigerer ist als derjenige der roten Späne, durch Saigerprozesse trennen, für welche verschiedene Ausführungsarten patentiert sind und angewandt werden.

Auf Veranlassung des Professor Borchers unternahm ich, nachdem auch elektromagnetische Versuche wegen der gegenseitigen Verfilzung der Drehspäne untereinander keine befriedigenden Ergebnisse geliefert hatten, Scheidungsversuche auf chemisch-metallurgischem Wege.

In der Mischung enthielten

die weißen Späne . .	84% Sn	10% Sb	6% Cu
die roten Späne . . .	10 „ „	0 „ „	90 „ „

Das Gemisch wurde geschmolzen, damit für die Versuche ein Material gleichmäßiger Zusammensetzung vorlag. Die erkaltete Schmelze bildete eine spröde, leicht pulverisierbare Masse von folgender Zusammensetzung:

Cu 56,10%	Sb 3,36%
Sn 33,94 „	Pb 3,23 „

Die übrigen Bestandteile sind Fe und Zn.

Nachdem früher im Aachenischen Laboratorium ausgeführte Scheidungsversuche von Blei-Zinnlegierungen gute Ergebnisse geliefert hatten, wurde versucht, durch

Verbleiung und oxydierendes Schmelzen

eine Scheidung des Kupfers von den übrigen Bestandteilen zu erzielen. Die Ergebnisse dieser Arbeiten waren wenig befriedigend; denn erst bei einem Verhältnis von Blei zur Legierung=4 : 1 wurden einigermaßen flüssige Schlacken erhalten; aber trotzdem kam ich auf eine Kupferausbeute von nur 36 bis 37% des Kupfergehaltes.

Um keine Zeit mit der Bildung von Glätte zu verlieren, wurde dann die pulverisierte Legierung bei einem weiteren Versuche unmittelbar mit Bleiglätte und schließlich mit einem Gemisch von Bleiglätte und Soda verschmolzen zu dem Zwecke, gleich von vornherein eine stark basische, die Lösungsgeschwindigkeit von Zinn und Antimon erhöhende Schmelze zu schaffen.

Das hierbei fallende kupferhaltige Blei, sowei aus diesem ausgesaigertes metallisches Kupfer waren vollständig frei von Zinn und enthielten nur noch Spuren von Antimon; die Schlacken aber enthielten beträchtliche Mengen von Kupfer, gleichzeitig aber das Antimon und Zinn in fast unlöslichem Zustande.

Auch Versuche, nach dem Verfahren von Borchers und Peetz wenigstens eine

Scheidung des Zinnes auf elektrolytischem Wege

in der Weise herbeizuführen, daß die Legierung als Anode in wässeriger Alkalilauge als Elektrolyt gegenüber einer Kathode aus Bleioxyd ohne äußere Energiezufuhr angeordnet wurde, erwies sich für diesen Fall ebenfalls erfolglos. Die Lösungsgeschwindigkeiten von Zinn und Antimon wurden durch die übrigen Bestandteile der Legierung derartig herabgemindert, daß eine Anwendung dieses Verfahrens ausgeschlossen war.

Bessere Aussicht auf Verwendbarkeit bietet nach den Ergebnissen folgender Versuche.

Sulphierende Schmelzen mit anschließender Laugerei.

Als Sulphierungsmittel wurde Bleiglanz gewählt, von welchem das in den ersten sechs Versuchen angewandte Erz

82,57% Blei und 13,71% Schwefel

enthielt, während das für die übrigen Versuche gebrauchte Erz

82,00% Blei und 13,34% Schwefel enthielt.

Zur Ueberführung der in 100 Gewichtsteilen der Legierung enthaltenen Metalle waren somit erforderlich

auf	Schwefel zur Bildung von Cu_2S und SnS	Bleierz
Cu 56,13	14,1	108
Sn 33,94	9,1 [1]	70 [1]

1) Zur Bildung von SnS_2 bezw. Na_2SnS_3 würde natürlich die doppelte Menge von Schwefel oder Bleierz erforderlich sein.

Bei einer Reihe von Versuchen wurde angestrebt, durch gleichzeitige Erzeugung von Natriumsulfid in Wasser lösliche Sulfosalze zu erzeugen, um hiermit eine Trennung der Sulfide zu ermöglichen. Die gewählten Beschickungen sowie die Zusammensetzung der Schmelzprodukte finden sich in der folgenden Tabelle zusammengestellt:

Nr.	Beschickung in Gramm					Produkt							
						Rugulus							Stein
	Legierung	Pb-Erg.	Na_2SO_4	C	Glas	Gewicht in g	Gesamt-Sb in g	Sb-Gehalt in %	Gewinnung % vom Sb	Gesamt-Sn in g	Sn-Gehalt in %	Gewinnung % vom Sn	
1	100	110	—	—	5	Die Legierung zersetzt nicht vollständig							Immer zinnhaltig
2	100	120	—	—	5								
3	100	130	—	—	5								
4	100	110	40	12	—								
5	100	120	40	12	—								
6	100	130	40	12	—								
7	100	140	—	—	5	130	3,30	2,47	98,2	22,68	17,45	66,8	
8	100	140	40	12	—	134	3,33	2,48	99,1	15,00	11,19	44,2	
9	100	200	92	28	—	135	3,34	2,48	99,3	5,54	4,10	16,3	
10	100	250	80	20	20	155	3,33	2,15	99,1	6,08	3,92	17,9	
11	100	300	80	20	20	159	3,08	1,94	91,7	6,03	3,79	17,8	
12	100	350	80	20	20	178	2,82	1,58	83,9	6,71	3,77	19,8	

Das Metall von Versuch 7 enthielt 3,9 g Cu, nämlich 2,86% vom Gesamt-Cu in Legierung; die Metalle der Versuche 8, 9, 10, 11, 12 enthielten nur Spuren von Cu.

Aus diesen Zahlen läßt sich folgendes ableiten:

1. Von den Bestandteilen der Legierung geht zwar das Kupfer am schnellsten und vollständigsten in Sulfid über, gleichzeitig aber erhebliche Mengen Zinn schon lange ehe die Hauptmenge Kupfer sulfiert ist.

2. Mit steigendem Natriumsulfidgehalt der Schmelze vergrößert sich die Lösungsgeschwindigkeit des Zinnes in geschmolzenen Sulfiden.

3. Die Lösungsgeschwindigkeit von Antimon in Blei ist größer als in geschmolzenen Sulfiden.

Aus dem erhaltenen Stein ließen sich durch verdünnte Natriumsulfidlösungen 93% des darin übergegangenen Zinnes lösen, während das Kupfer vollständig ungelöst zurückblieb.

Eine Scheidung des Kupfers und der größeren Menge des Zinnes aus der Legierung in Form leicht weiter verarbeitbarer Sulfide wäre daher denkbar, wenn auch ein nicht unerheblicher Teil des Zinnes von dem erschmolzenen Blei zurückgehalten wird. Die Verarbeitung zinn-und antimonhaltigen Bleies unter Gewinnung des Zinnes wird bekanntlich auf einzelnen Bleihütten durchgeführt, so daß dieser Teil des Zinnes keineswegs verloren ist.

Bemerkenswerte Vorteile gegenüber den bekannten Saigerungsprozessen würden die bei den vorstehenden Versuchen eingeschlagenen Wege nicht bieten. Die Saigerprozesse liefern das ausgesaigerte Weißmetall ebdnsowenig wie die zurückbleibenden Rotspäne in dem Zustande ihrer früheren Reinheit, aber doch so, daß beide nur mit geringen Metallverlusten in verwendbare Formen gebracht werden können. Immerhin habe ich eine Mitteilung dieser Versuchsergebnisse für angezeigt gehalten, da nicht nur erfolgreiche Versuche lehrreich sind.

Formation of Amines from the Halogen Imido Esters.

By

Mitsuru Kuhara and **Motooki Matsui.**

The mechanism of well-known Hofmann's reaction for the formation of amines from the acid bromamides, has been, for its final solution, one of the most interesting of problems; and thus far it has been looked upon as parallel with so-called Beckmann's rearrangement.

Hoogewerff and van Dorp[1] assigned to the alkali salts of the acid bromamides, the constitution, RCO(NM'Br), and first pointed out the analogy between the mechanism of Hofmann's reaction and that of Beckmann's rearrangement.[2] The latter, as is well known, is dependent upon the mutual exchange between the position of the halogen atom combined with nitrogen and that of the hydrocarbon radical linked to carbon, in a compound possessing a double union between those carbon and nitrogen atoms, as is seen in the following scheme:

$$\begin{array}{c} R-C-R' \\ \| \\ X-N \end{array} \longrightarrow \begin{array}{c} X-C-R' \\ \| \\ R-N \end{array}$$

Admitting that the constitution of the alkali salts of the acid bromamides, proposed by Hoogewerff and van Dorp, is true, a close analogy can hardly be recognised between both mechanisms. It was shown, however, by Stieglitz and Ransom[3] on the one

[1] Rec. trav. chim., **6**, 373; **8**, 173.
[2] Ber. d. chem. Ges., **19**, 988; **20**, 1807, 2580.
[3] Ibid., **34**, 1615.

hand, and by Hantzsch[1] on the other, with different methods of experimentation, that the alkali salts of the acid bromamides should possess a constitution different from that originally given by the Dutch chemists, and is assignable the new constitution which must belong to a series of the salts from the pseudo-acids, so-called by Hantzsch; as is seen:

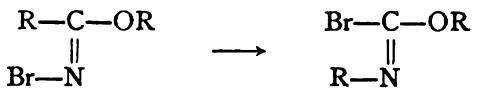
With such a representation of the constitution of the salts of the acid bromamides, a complete analogy is apparent between Hofmann's reaction and Beckmann's rearrangement:

Moreover, the fact that Hofmann's reaction takes place only in the alkaline solution of the bromamides, (that is, only with their alkali salts, but not with the free bromamides), gives support to Hantzsch's view,[2] that the free bromamides contain no double linking between the carbon and nitrogen atoms, while in the alkali salts of the bromamides as pseudo-acids, a double linking is effected, essentially by alkali bringing them into close analogy with oximes. Stieglitz,[3] noticing the possibility of a double linking to be an essential condition of the rearrangement, carried out the investigation of the halogen imido esters for their rearrangement, which is possible, arguing from the analogy apparent between the newly assigned constitution of the alkali salts of the acid halogen amides and that of the halogen imido esters, as shown below:

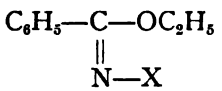
[1] Ber. d. chem. Ges., **35**, 226.

[2] Ibid., **35**, 3579.

Amer. Chem. Journ., **18**, 751; **29**, 49.



He found, however, that the halogen imido esters, such as chlorimido and bromimido ethyl benzoates—$C_6H_5.C(NCl)OC_2H_5$ and $C_6H_5.C(NBr)OC_2H_5$—do not undergo Beckmann's rearrangement by the action of heat, simply yielding benzonitrile as the chief decomposition product, but are decomposed into benzoic ether and hypochlorite or hypobromite by the action of hydrochloric acid. Hence the conclusion was drawn by him that the chlorimido or bromimido ethyl benzoates are, possibly, anti compounds, as is shown below:



The authors have been induced to the notion that, if chlorimido and bromimido esters had the configuration of the anti form, as Stieglitz states, the alkali salts of the acid halogen amides, which are possible to be formed by their saponification, would not undergo Beckmann's rearrangement, for they ought to take the same configuration as the esters. Nevertheless, it was observed by the authors that much amines are formed from those esters by the action of alkali, under the same conditions as in the formation of amines from the acid bromamides by alkali, as Hofmann describes. In the experiments, bromimido ethyl acetate, propionate, and benzoate—$CH_3.C(NBr)OC_2H_5$, $C_2H_5.C(NBr)OC_2H_5$ and $C_6H_5.C(NBr)OC_2H_5$—were taken, and each ester was digested with a solution of caustic potash for some time, by gentle heating; afterwards the mixture was distilled, the distillate being received into hydrochloric acid. On evaporating the acid solutions, the respective amines, CH_3NH_2, $C_2H_5NH_2$ and $C_6H_5NH_2$, were obtained in the residues, as their hydrochlorides mixed with much ammonium chloride.

With regard to the formation of amines from the respective

halogen imido esters, the authors put forward their explanation upon the assumptions to be hereinafter stated:

It is virtually evident that the halogen imido esters possess the configuration of the anti form, by inference from Stieglitz's view[1] as already described; and, moreover, from the stereochemical standpoint for the formation of the imido esters from nitriles and alcohols.

Applying Abegg's conception for the stability of stereoisomeric oximes in alkaline solution,[2] to the acid halogen amides, it is conceivable that the latter in alkaline solution, owing to the presence of the group, C—OK, as the salts of pseudo-acids, may play a part of anion in the case of electrolytic dissociation, the electrical charge being plausibly considered to be localised at —O′. Since they may take two different configurations of syn and anti forms:

Anti form, (Unstable). Syn form, (Stable).

and the radicals X and R are differently charged with electricity, the production of stable and unstable forms is possible, owing to the attraction between X and R on the one hand, and the repulsion between X and —O′ on the other.

Now, it is highly probable that the halogen imido esters of the anti form, when heated with caustic potash, may change to the potassium salts of the halogen imido acids of the same form by saponification, which will immediately change to the salts of the stable syn form and consequently undergo the Beckmann rearrangement, followed by their decomposition into amines by the further action of the alkali present. The scheme of transformation may be represented thus:

[1] Loc. cit.

[2] Ber. d. chem. Ges., 32, 291.

$$\begin{array}{c} R-C-OC_2H_5 \\ \| \\ N-Br \end{array} \longrightarrow \begin{array}{c} R-C-OK \\ \| \\ N-Br \end{array} \longrightarrow \begin{array}{c} R-C-OK \\ \| \\ Br-N \end{array} \longrightarrow \begin{array}{c} Br-C-OK \\ \| \\ R-N \end{array}$$

Acting upon such an assumption, the authors have come to the conclusion that the alkali salts of the acid bromamides as pseudo-acids, always possess the syn form, which may be the only form of the alkali salts capable of existence, consequently undergoing rearrangement readily and then effecting the decomposition into amines; and they further conclude that this is one of the reasons why the acid bromamides undergo the rearrangement and decomposition only in the form of alkali salts.

EXPERIMENTAL PART.

1. Bromimido Ethyl Acetate, $CH_3.C:NBr.OC_2H_5$

For its preparation, a cooled solution of potassium hypobromite, prepared by dissolving a calculated quantity of bromine to a 10% solution of potassium hydroxide, was gradually added to imido ethyl acetate prepared by the method suggested by Pinner,[1] with constant stirring until the solution assumed permanently a yellow colour. The oily bromimido ethyl acetate thus obtained was yellow in colour. It was well shaken with a dilute solution of potassium hydroxide, washed with water and dehydrated over fused calcium chloride. Its behaviours toward water, acids, and alkalies have been studied.

It is very unstable in the presence of water, the liberation of bromine being effected even in a moist state, and the reaction being likely to be the reverse of that in its formation, as Stieglitz[2] has already observed with bromimido ethyl benzoate:

$$CH_3.C:NBr.OC_2H_5 + H_2O = CH_3.C:NH.OC_2H_5 + HBrO$$

At a high temperature, the reaction seems to go on further: on heating it with water over a water-bath, acetic ether was observed

[1] Ber. d. chem. Ges., **16**, 1654.
[2] Amer. Chem. Journ., **18**, 761.

to distil over, together with bromine, leaving the ammonium salts behind as residue. Thus the reaction may be formulated as follows:

$$CH_3.C:NBr.OC_2H_5 + 2H_2O = CH_3.COOC_2H_5 + NH_4BrO$$

It gives a gaseous substance which strongly attacks the eyes and nose, reminding us of isocyanate, especially when heated with water, the same phenomena being observed as with the other bromimido esters; the authors were, however, unable to ascertain whether the smell is that of the bromimido ester itself or of some decomposition products.

It is very unstable against the action of acids readily liberating bromine. When the ester was heated with some hydrochloric acid, acetic ether was observed to distil over, together with bromine, leaving ammonium chloride as the residue on continuing the distillation to complete dryness. The authors give the following equation as the explanation of the reaction:

$$2CH_3.C:NBrOC_2H_5 + 2HCl + 2H_2O$$
$$= 2CH_3.COOC_2H_5 + 2NH_4Cl + Br_2 + Cl_2$$

In order to study its behaviour toward alkali, it was mixed with a large excess of a 30% solution of potassium hydroxide in a flask, provided with a delivery tube which dipped into hydrochloric acid, and heated gently until the oily ester disappeared, and then the whole content was subjected to distillation, some alcohol having been observed to pass over before the evolution of the methylamine. The acid solution was evaporated to dryness over a water-bath, and the residue tested by Hofmann's reaction for the presence of methylamine hydrochloride, and in fact gave the offensive smell of isonitrile. The residue was now treated several times with absolute alcohol to separate the methylamine salt from ammonium chloride. The salt thus obtained was converted into the platinum double salt and analysed:

0·3424 grm. the double salt gave 0·142 grm. platinum on ignition.

	Found.	Calc. for $2(CH_3NH_2HCl).PtCl_4$.
Platinum	41·47	41·25

The yellow coloured alkaline aqueous part produced in the preparation of the bromimido ester was carefully separated from the oily part by filtration, and distilled with the addition of more potassium hydroxide, in which process the production of methylamine was observed. Hence it is probable that some of the bromimido ester of the anti form may have changed into the potassium salt of bromimido acid of the syn form, which was present in the solution in a state favourable to undergo rearrangement and in consequence to effect the decomposition into methylamine.

2. Bromimido Ethyl Propionate, $C_2H_5.C:NBr.OC_2H_5$

This was prepared from imido ethyl propionate and experimented on in a way similar to that followed in the case of bromimido ethyl acetate, and its behaviour was, likewise, found to be analogous to that of the latter. The amine formed from the ester, was observed to be ethylamine by the analysis of its double salt of platinum:

0·3014 grm. the double salt gave 0·1194 grm. platinum on ignition.

	Found.	Calc. for $2(C_2H_5NH_2HCl).PtCl_4$.
Platinum	39·62	38·98

3. Bromimido Ethyl Benzoate, $C_6H_5.C:NBrOC_2H_5$

This was prepared from bromimido ethyl benzoate and investigated in the ways similar to those followed with the aforementioned esters. Besides the behaviour already observed by Stieglitz,[1] as well as that perceived by the authors as common to the halogen imido esters, the characteristic noticed in this ester is its action on water: on standing in a moist state for a few days, a quantity of cyaphenine crystallised out, with the liberation of bromine and the formation of benzoic ether. The authors venture to interpret

[1] Amer. Chem. Journ., **18**, 760.

the reaction in the following ways: at first water may regenerate the imido ester and the latter, so formed, change to cyaphenine,[1] simultaneously some of the imido ester acting upon water so as to form benzoic ether, thus:

$$C_6H_5.C:NBrOC_2H_5 + H_2O = C_6H_5.C:NH.OC_2H_5 + HBrO$$
$$C_6H_5.C:NH.OC_2H_5 + H_2O = C_6H_5.COOC_2H_5 + NH_3$$

Aniline hydrochloride obtained from bromimido ethyl benzoate by the action of alkali, was analysed:

0·3982 grm. the double salt gave 0·13 grm. platinum on ignition.

	Found.	Calc. for $2(C_6H_5NH_2HCl).PtCl_4$.
Platinum	32·65	32·70

[1] Ber. d. chem. Ges., **22**. 1611.

November, 1906.

Note on the Refining of Copper.

By

Daikichi Saito.

Professor E. Heyn published the results of his investigations, about four years ago, with regard to the manner in which oxygen exists in copper.[1] He explained it both chemically and metallographically, showing that copper with about 3·5% Cu_2O, has so-called 'eutectic structure' and the lowest melting point in a series of the alloys of copper and oxygen. Subsequently, in 1903, H. O. Hofman, C. F. Green and R. B. Yerxa, at the New York meeting of the American Institute of Mining Engineers, reported the results of a laboratory study of the stages in the refining of copper.[2] They determined the oxygen content of the different kinds of American copper, and gave photographs of their fracture and microstructure, proposing the planimetrical measurement of the oxygen content in copper; but it was not a systematic study of the copper refining process.

The author contemplated pursuing more systematically the process of dry refining, in some investigations made upon the blister copper from the Beshi mine, in this country; refined copper from which is so renowned for its purity in the European markets.

Let us consider the investigations under several headings, as follows:

[1] Mittheil. aus der königl. Versuchanst. zu Berlin, 1900, XVIII, 315.
[2] Trans. Amer. Inst. Min. Eng., 1904, XXXIV, 671.

I. Rough Sketch of the Smelting Process at the Beshi Copper mine.

The ore smelted at the Beshi works is a cupriferous iron pyrites, whose copper content varies between 3% and 10%, averaging about 5%. It is almost free from injurious impurities. The ore is roasted in stalls and smelted in blast furnaces to get the raw matte of about 30% copper content; the latter is again roasted and smelted for the concentrated matter of about 65% copper content. The molten concentrated matter is charged into reverberatory furnaces of nine tons capacity each, and is worked for blister copper. These furnaces work under a blast of 5 lbs. per square inch, blown obliquely against the surface of the molten bath. This process is a kind of blast refining developed in this country, and is called "Atebuki."

The blister copper thus produced is comparatively pure: as is shown in the following table:

98·970%	Copper.
0·220%	Oxygen.
0·043%	Sulphur.
0·077%	Iron.
0·091%	Charcoal and insoluble matter mechanically mixed.
99·401%	

The remaining part consists of other impurities, such as nickel, antimony, etc.

II. Mode of the Refining of the Blister Copper.

The refining is conducted in a reverberatory furnace of about fifteen tons capacity, using coal as fuel. The total time taken for remelting and refining, lasts for about 17½ hours: further details of the process and of the time of sampling are given in the following table.

Table I.

No. of Samples.	Time of Sampling.	Duration of Heating.	Duration of Rabbling.	Duration of Poling.	Remarks.
I.	4.40 P.M., 6, 28, 1906.	6 h. 50 m.*			Blister copper before remelting.
II.	11.30 P.M.				Blister copper after remelting.
III.	1.30 P.M., 6, 29, 1906.	2 h. 00 m.			At the beginning of the first rabbling.
IV.	2.30 A.M.		1 h. 00 m.		One hour after the beginning of the first rabbling.
V.	3.30 A.M.		1 h. 00 m.		At the end of the first rabbling.
VI.	4.00 A.M.	0 h. 30 m.			At the beginning of the second rabbling.
VII.	5.00 A.M.		1 h. 00 m.		One hour after the beginning of the second rabbling.
VIII.	6.00 A.M.		1 h. 00 m.		At the end of the second rabbling.
IX.	6.30 A.M.	0 h. 30 m.			At the beginning of the third rabbling.
X.	7.30 A.M.		1 h. 00 m.		One hour after the beginning of the third rabbling.
XI.	8.30 A.M.		1 h. 00 m.		At the end of the third rabbling.
XII.	9.00 A.M.	0 h. 30 m.			Before the first poling.
XIII.	9.30 A.M.			0 h. 30 m.	After the first poling.
XIV.	10.15 A.M.			0 h. 45 m.	After the second poling (i.e. finished product).
		10 h. 20 m. +	6 h. 00 m. +	1 h. 15 m. =	17 h. 35 m., Total time for refining.

* For remelting.

As shown in the table, the author obtained fourteen samples

from the works to be analysed, and determined the amounts of various elements present in them.

III. Determination of Various Elements in the Copper.

The determination of small amounts of various elements in commercial copper, is a pretty difficult task. The author chiefly took, for reference, A. Classen's work[1] and W. Hampe's paper.[2] Some modifications were made in order to secure more accuracy.

A. *Determination of Total Oxygen present in Copper.*

The author adopted Hampe's method[3] with some modifications for catching the sulphur which escapes as hydrogen sulphide from the copper by the current of hydrogen. The apparatus for this determination consists of the following separate parts, which are connected together in a series.

a) A Kipp's gas generator, charged with granulated zinc and dilute hydrochloric acid (1 : 1), to generate hydrogen for reduction.

b) A wash bottle with an alkaline solution of lead to catch the hydrogen sulphide gas which may happen to be present in the gas.

c) Two U-tubes containing calcium chloride for drying the gas.

d) A Bohemian glass tube, 1″ thick and 18″ long, provided with a well fitted cork stopper with a delivery glass tube: it is charged with two porcelain boats filled with copper borings, and placed in a glowing furnace heated by gas.

[1] A. Classen, Ausgewählte Methoden der analyt. Chemie. Bd. I. 96.
[2] Pr. Zeit. B. H. Salinenwesen, 1873, XXI, 231.
[3] Loc. cit.

e) A small Erlenmeyer flask of 100 c.cm. capacity, containing cadmium acetate solution acidified with acetic acid.[1] The gas from the reduction tube is passed through the solution, which will catch all the sulphur escaping from the copper as hydrogen-sulphide.

The manner of experimentation is as follows: samples are taken from the individual specimens by slow boring, and the small particles of iron which may come from the bits are removed with a magnet. These borings are washed first with absolute alcohol and then with ether, twice respectively; when perfectly dry, they are stored in well stoppered bottles.

13–20 grams the samples are accurately weighed and charged into two previously annealed and weighed porcelain boats. These charged boats are introduced into the glass tube already described, and the parts of the apparatus are then connected together and tested for air tightness.

The purified and dried hydrogen gas is then passed through the apparatus for about thirty minutes to expel the air, and the glass tube loaded with the sample boats is gradually heated, the current of the hydrogen gas being constantly passed. The temperature is raised to a bright red heat (sintering temperature of copper). When it rises, the oxygen in the copper is acted upon by the hydrogen gas and the water which is formed partly condenses at the cooler part of the tube. But it is a singular fact that sulphur in copper is first given off when the greater part of the oxygen has passed away; that is, after about thirty minutes glowing, sulphur presents itself in the cadmium solution as the yellow precipitate of cadium sulphide.

After about two hours glowing when the reduction of the copper oxide has completed, the flame is gradually lowered and the apparatus cooled down in the current of hydrogen gas. When perfectly cooled, the porcelain boats, charged with copper are taken out, placed in a dessicator, and then weighed. The loss

[1] A. Ledebur-Leitfaden f. Eisenhütten-laboratorien, 1903, 105.

of weight shown by the weighings of the boats, gives the amount of oxygen and sulphur driven out by the ignition. In order to ascertain the exact amount of oxygen driven off, we must determine the quantity of sulphur caught by the cadmium acetate solution: this is done by Schult's method.[1] The quantity of sulphur having been thus found, its weight is subtracted from the total loss in weight determined as before, and we now get the nett amount of oxygen in the copper.

B. *Determination of Sulphur in Copper.*

It would have been very convenient if we could have expelled the total amount of sulphur in copper as hydrogen sulphide by heating it to the glowing point in the current of hydrogen, and determined its amount simultaneously with the oxygen. The author tried several times to do so, but found that the reaction was never complete, and the results were always too low and variable. Accordingly, he followed the usual barium sulphate method.

He took 15–20 grams the sample for one determination and dissolved it slowly in nitric acid (1·2), oxidised and filtered, and the sulphuric acid thus formed was precipitated as $BaSO_4$ by barium chloride in hot state; and so forth. But he wonders that some of the sulphur may have escaped as sulphur dioxide gas during the process of dissolving, as the results were somewhat too low.

C. *Determination of Iron in Copper.*

According to Classen and Hampe, the determination of small quantities of iron in copper is rather a complicated process. In the author's experiments, the copper was fairly pure and almost free from the elements of the first and second groups, so he employed the method described as follows:

[1] A. Ledebur-Leitfaden f. Eisenhütten-laboratorien, 1905, 109.

Dissolve 15–20 grams the sample in nitric acid (1·2), add some sulphuric acid and evaporate almost to dryness to drive off the first named acid. The sulphate solution now prepared is subjected to electrolysis: a copper plate as cathode and a platinum plate as anode, and an electric current of about 1·5 amp. at 2·5 volts is passed over a night.

In the morning, all the copper, or almost all of it, is deposited on the cathode, while the iron remains in solution as ferrous salt. Now add a few drops of bromine and heat, to oxidise it to ferric salt, and then ammonium chloride and an excess of ammonia to precipitate the iron as hydroxide. After the solution has then been allowed to stand for at least ten hours, it is filtered and analysed by the gravimetric method.

D. *Determination of Metallic Copper.*

The electro-analysis in a nitric acid solution, proposed by Classen, was adopted. The details of the process are given in his text-book.[1] It gave an excellent result.

Altogether, the author conducted at least two or three determinations for each element; and he took the average of the two most probable results for graphic tabulation. But he confesses that the results of the sulphur determination may have been somewhat inaccurate, owing chiefly to the minuteness of its quantity; in the results of the iron analysis, also, we found some irregularities. The latter may probably be due to the imperfect sampling: that is, from the difficulty of completely extracting the iron particles from the samples with a magnet.

IV. Results of Analysis.

The results of the chemical analysis of the fourteen samples are tabulated as follows:

[1] A. Classen: Quantitative Analyse durch Electrolyse, 1897, 168.

Table II.

No. of Sample.	Copper.	Oxygen.	Sulphur.	Iron.
I.	98·970%	0·220	0·0426	0·077
II.	99·350	0·410	0·0116	0·058
III.	99·403	0·450	0·0045	0·043
IV.	99·401	0·500	0·0035	0·034
V.	99·400	0·510	0·0030	0·028
VI.	99·357	0·629	0·0023	0·030
VII.	99·230	0·728	0·0021	0·033
VIII.	99·160	0·836	0·0019	0·027
IX.	99·100	0·898	0·0023	0·028
X.	99·012	0·980	0·0010	0·025
XI.	98·910	1·103	0·0015	0·023
XII.	98·720	1.235	0·0012	0·025
XIII.	99·795	0.089	trace	0 020
XIV.	99·828	0·050	trace	0·022

Based upon the results stated here, the author has drawn a diagram which will be annexed at the end of the article. The abscissa represents the time in hours and minutes, at which intervals fourteen samples were taken. The ordinate represents the amount of various elements, one division corresponding to 0·5%: for copper only, the ground line to 98% and proceeding upwards in the same ratio as the others.

V. Summary.

1. If we trace the oxygen curve, it will be observed that, up to the end of the first rabbling, i. e. the sample V, the oxygen content of the molten copper rises very slowly from 0·22% to 0·51% in ten hours and fifty minutes: in this period, the greater part of the impurities are oxidised.

From this point up to the end of the third rabbling, i. e. the sample XII, the oxygen absorbed is used to oxydise the remaining impurities; but the major part of it oxidises the copper itself, and its content reaches the maximum, 1·23% in the sample XII.

Now begins the first poling (reduction), and after thirty minutes the oxygen content falls abruptly to only 0·089%, as in the sample XIII, and after the second poling, oxygen falls only through 0·039% up to 0·05% in the finished product.

2. Next trace the copper curve: from the sample I to the sample II, the copper content rises gradually, and from the sample II to the sample V it remains almost constant; but from this point, it begins to sink very rapidly up to the end of the third rabbling, corresponding to the sudden increase of oxygen: that is from 99·40% to 98·72%.

After a short time of poling, its content rises abruptly, as a consequence of the sudden decrease of oxygen content, till after the second poling, when its content reaches 99·828%.

3. The original content of sulphur in the copper is very low, amounting to 0·0426%, and after remelting it sinks to only 0·0116%, as in the sample II. But it is probable that the copper absorbs some sulphur from the combustion gas during remelting at lower temperatures, and there would have been some rise in the curve between the samples I and II, if we could have taken out the sample. On the whole, the sulphur content is already reduced almost to a trace after the first rabbling, i. e. in sample V.

4. The iron content in the original blister copper is also very low, amounting to only 0·077%, and oxidised as the refining proceeds; still in the finished product we find 0·022%. As shown in the analytical table already given, the iron content has some irregularities; and therefore it is not traced on the diagram.

But the author believes that the iron content falls gradually, from the maximum to the minimum, as the refining proceeds without any undulations.

5. Summing up the above results, we now turn to the practical side. As will be seen by an inspection of the diagram, in the refining of such comparatively pure blister copper as this, the greater part of its impurities is oxidised in the early stages of refining; i. e., after the end of the first rabbling, the copper contains only about 0·03% iron and 0·003% sulphur, and after the second

rabbling, the iron content remains nearly unchanged; while the copper is practically free from sulphur.

The author doubts if it is necessary to prolong the remelting period as this, or to continue the oxidising action so long. If the copper could be remelted much quicker, and the third rabbling period be cut out, then there would be a great economy in fuel consumption and in labour.

Next, in the author's experience, the effect of the first poling is so great that the second poling seems to be unnecessary. Of course, this condition varies according to the state of the furnace and with the manner of working; but he believes that, at least, the time of the second poling can be shortened, and something be saved both in fuel and in labour.

The author avails himself of this opportunity to thank Mr. K. Nakamura, chief engineer of the metallurgical department of the Beshi mine, for his kindness in supplying the samples required for these experiments.

October, 1906.

1.00%

0.60%

0.22%C

0.0426%S

0%

Electrolytic Dissociation of Partially Neutralised Weak Acids.[1]

By

Yûkô Mori.

In the last number of these Memoirs, Professor Osaka[2] described the deduction he had arrived at as to some relationship in the electrolytic dissociation of weak monobasic acids which have been partially neutralised with a strong monoacid base. At his suggestion, the author has undertaken experimental verification of such relations, and some of the results obtained will be stated below.

I. When a dilute solution of a weak monobasic acid has been neutralised by half with a strong monoacid base, the concentration of the hydrogen ions is independent of dilution and equal to the dissociation constant of the acid.

For the experimental verification of the relationship, acetic and benzoic acids were taken, and each was neutralised by one-half with sodium hydroxide. The concentration of the hydrogen ions in the solution was estimated in a manner similar to that which Trevor[3] had followed in the case of bibasic acids, by means of their catalytic action in the inversion of cane sugar at the temperature of boiling water. The experiments were carried out as follows:

[1] The experimental work was done in the spring of the year 1905.

[2] These Memoirs I., No. 2, 103.

[3] Zeitschr. f. physik. Chem., 10, 331 (1892).

10 c. c. of a solution of known composition were mixed with an equal volume of a cane sugar solution of 12 per cent., and polarised at 25° C. The solution was transferred to test tubes of silver and of hard glass, which were stoppered with corks provided with long capillary tubes, and dipped into a bath of boiling water for a definite period of time, then cooled suddenly, and again polarised at 25° C. The results of the experiments conducted with a silver tube and those with a hard glass tube, showed no remarkable difference, and the solution in each tube sustained no loss by evaporation during the experiment.

The concentration of the hydrogen ions in the solution was calculated from the results of the polarimetric observation by the following equation:

$$\log \frac{A}{A-x} = kt = k' C_H t;$$

where A represents the initial concetration of the cane sugar; x its decrease by inversion in the time, t; k the velocity constant of inversion for a given concentration of hydrogen ions C_H, and k' that for its unit concentration. According to Trevor, k' at 100° C. is 17·92. In the present experiment, however, the temperature varied between 99·8° and 99·6°, and the value of k' for the mean temperature, 99·7°, was estimated approximately as 17·6, from the above given value by Trevor and that of Arrhenius[1] 0·375 for 54·3° C. With the application of this constant, the concentration of the hydrogen ions will be given by the formula:

$$C_H = \frac{k}{17{\cdot}6}$$

The influence of neutral salts on the catalytic action of hydrogen ions is neglected in this formula, and in such dilute solutions as those used in the present experiments, this approximation will exert no remarkable influence upon the results.[2]

The concentration of cane sugar A and $A-x$ were evaluated

[1] Zeitschr. f. physik. Chem., 5, 2 (1890).

[2] Cf. Arrhenius, l. c.; Lippmann, Chem. d. Zuckerarten, II., 1280; etc.

in the following way: Let R be the angle of the dextro-rotation of a sugar solution; L be that of the levo-rotation of the same solution, when the inversion has been completed; and W be that of the dextro-rotation at the time t, then we may put:

$$A = R + L \quad \text{and} \quad A - x = L + W.$$

The value of L corresponding to R taken as 100·00° at a given temperature ϑ may be calculated by the formula[1]: $44{\cdot}16 - 0{\cdot}506\,\vartheta$. In the present experiments, R was always 8·00°, then $L = 2{\cdot}52$ and therefore $A = 10{\cdot}52$.

In the case of acetic and benzoic acids in several dilutions respectively being neutralised by one-half with sodium hydroxide, the following results were obtained:

Table I.

Acetic acid.

Dilution in litres.	Time in min.	W. (1)	W. (2)	W. (3)	W. Mean.	$A-x$.	k. 10^4.	C_H. 10^5.
100	186	6·92°	6·87°	6·89°	6·89°	9·41	2·60	1·48
200	,,	7·00	6·91	6·95	6·95	9·47	2·40	1·36
400	,,	6·94	7·00	6·90	6·91	9·43	2·55	1·45
800	,,	7·00	6·91	6·98	6·96	9·48	2·43	1·38
							Mean	1·42
			Benzoic acid.					
200	180	4·74°	4·73°	4·73°	4·73°	7·25	8·76	4·98
400	,,	4·71	4·70	4·70	4·70	7·22	9·07	5·15
800	,,	4·91	4·86	4·86	4·88	7·40	8·28	4·71
							Mean	4·95

As is seen in the table, the concentration of the hydrogen ions in each case, is independent of dilution, preserving good harmony with theory. Moreover, the theory requires that this concentration shall be equal to the dissociation constant of the acid. Measuring the electrolytic conductivity of acetic and bonzoic

[1] Landolt, Opt. Drehungsvermögen, 179 (1879).

acids, Ostwald[1] ever found their dissociation constants, at 25° C., to be $1{\cdot}80.\ 10^{-5}$ and $6{\cdot}0.\ 10^{-5}$ respectively; and Arrhenius[2] that of acetic acid at 54·3° C. to be $1{\cdot}615.\ 10^{-5}$. According to Euler,[3] the dissociation constant of benzoic acid varies with temperature, having a maximum as follows:

Temperature.	0°	20°	25°	30°	40°	50°
$K.\ 10^5$	6·05	6·64	6·69	6·72	6·72	6·65

While according to Bauer[4] that at 25° C. is $7{\cdot}3.\ 10^{-5}$. Thus, these constants observed for both acids as such by other chemists are much greater than those found by the author himself. Such deviation may, perhaps, be due to a wide difference of temperature.

II. When a dilute solution of a weak monobasic acid is neutralised by one-third with a strong monoacid base, the concentration of the hydrogen ions is independent of dilution, and equal to twice the dissociation constant of the acid.[5]

The experiments were carried out in a way similar to that pursued in the previous case, and results were obtained as follows:

Table II.

Acetic acid.

Dilution in litres.	Time in min.	*W.* (1)	*W.* (2)	*W.* Mean.	$A-x$.	$k.\ 10^4$.	$C_H.\ 10^5$.
100	186	5·81°	5·86°	5·84°	8·36	5·36	3·04
200	,,	5·83	5·81	5·82	8·34	5·42	3·08
400	,,	5·80	5·87	5·84	8·36	5·36	3·04
800	,,	5·90	5·91	5·91	8·43	5·17	2·93
						Mean	3·02

[1] Zeitschr. f. physik. Chem., **3**, 174 and 246 (1889).

[2] Ibid., **4**, 96 (1889).

[3] Ibid., **21**, 257 (1896).

[4] Ibid., **56**, 219 (1906).

[5] This follows naturally from the general equation given on page 103 of these Memoirs.

Benzoic acid.

Dilution in litres.	Time in min.	W. (1)	W. (2)	W. Mean.	$A-x$.	k. 10^4.	C_H. 10^5.
200	180	3·07°	3·01°	3·04	5·56	15·4	8·7
400	,,	3·03	3·22	2·13	5·65	15·0	8·5
800	,,	4·05	4·08	4·07	6·59	11·3	6·4

As is seen in the table, the concentration of the hydrogen ions, in the case of acetic acid, is here likewise independent of dilution; but with benzoic acid, it shows some variation, especially when the dilution is comparatively high. This deviation may, possibly, be due to the fact that benzoic acid is stronger than acetic acid; for the theoretical equation $C_H = 2K$, has been derived from a more exact one:

$$C_H \frac{2K(1-\gamma)}{1+2\gamma}$$

under the assumption that γ, the degree of dissociation of the acid, and 2γ may be neglected as against 1 without any remarkable error resulting.

When the acid is neutralised by one-third, γ is naturally greater than when it is neutralised by one-half; and, moreover, as the more dilute the solution, the greater γ becomes: hence it is to be expected that C_H will become smaller, more or less sensibly, when the dilution become higher, provided that γ exerts a remarkable influence upon the result, as is the case with a strong acid.

In the case of acetic acid, as has been shown, no remarkable influence of γ was observed, and its dissociation constant has been calculated to be $1{\cdot}52 . 10^{-5}$, which does not differ much from what was found in the former case. In the subsequent calculations the mean of the two values, namely, $1{\cdot}47 . 10^{-5}$, will be taken as the dissociation constant of acetic acid at 99·7° C.

III. When a dilute solution of a mixture of two weak monobasic acids, in equivalent proportions, is neut-

ralised by one-half with a strong monoacid base, the total concentration of the hydrogen ions is independent of dilution, and equal to the square root of the product of the dissociation constants of the two acids.

For the verification of this proposition, a mixture of acetic and benzoic acids was taken, and the experiments were conducted in the manners similar to the foregoing ones. The results were as follows:

Table III.

Dilution in litres.	Time in min.	*W.* (1)	*W.* (2)	*W.* Mean.	$A-x$.	k. 10^4.	C_H. 10^5.
200	180	6·00°	5·97°	5·99°	8·51	5·12	2·91
400	,,	5·96	6·00	5·98	8·50	5·14	2·92
800	,,	6·01	5·97	5·99	8·51	5·12	2·91
						Mean	2·91

Thus the concentration of the hydrogen ions is independent of dilution, and is approximately equal to the square root of the product of the dissociation constants of the two acids: that is,

$$\sqrt{0{\cdot}147 \times 0{\cdot}495} \times 10^{-4} = 2{\cdot}7.\ 10^{-5}$$

as has been expected from the theory.

Ueber eine einfache Methode, den Grundton eines Klanges, dessen Höhe um eine Octave unsicher ist, zu entscheiden.

Von

Hanichi Muraoka.

Es ist eine häufig vorkommende Erscheinung, dass die Höhe des Grundtones eines Klanges um eine Octave unbestimmt bleibt. So bemerkt Helmholtz,[1] dass der als Violinist und theoretischer Musiker berühmte Tartini Combinationstöne alle um eine Octave zu hoch angegeben hat, während andererseits Henrici die Obertöne er Stimmgabeln um eine Octave zu tief angiebt.

Der Umstand aber, dass einerseits ein Musiker die absolute Höhe eines Tones für den practischen Zweck niemals gebraucht, und andererseits ein Physiker reichliche Auswahl feiner Methode zur Bestimmung der Schwingungsanzahl hat, so ist es wohl erklärlich, warum die Aufgabe, den Grundton eines Klanges einfach und schnell zu bestimmen, so weit ich die Literatur verfolgen kann, nie berührt worden ist.

Bei Gelegenheit einer akustischen Untersuchung kamen mir Fälle vor, wo solche schnelle Bestimmungen wünschenswert waren, um die jedesmalige umständliche Bestimmung der Schwingungsanzahl zu vermeiden und ich wurde zur Idee geführt *diese Aufgabe durch die Analyse des Klanges durch das blosse Ohr zu lösen.*

Frägt man sich nämlich nach dem Grunde, warum ein Ton um eine Octave, also um ein so grosses Intervall, unbestimmt

[1] Helmholtz, Tonempfindungen, fünfte Ausgabe S. 105.

bleiben kann, während das Ohr doch fähig ist, die geringste Differenz von zwei nahezu gleichen Tönen zu unterscheiden, so ist derselbe in der Mannigfaltigkeit der in den Klängen enthaltenen Teiltöne und deren Intensitäten zu suchen.

Zunächst sei angenommen, dass der fragliche Klang aus den sogenannten harmonischen Teiltönen zusammengesetzt sei, was zumeist der Fall ist. Dann wissen wir, dass die harmonischen Reihen zweier Klänge, deren Grundtöne um eine Octave entfernt sind, die folgenden sind:

(1)	1,	2,	3,	4,	5,	6,	7,	8,.....,
(2)		2,		4,		6,		8,.....,

wo die Zahlen die Verhältnisse der Schwingungsanzahlen bedeuten.

Wenn nun ein Klang (1) wie (2) klingt, so liegt der Grund darin, dass die höheren Teiltöne verhältnissmässig stark vertreten sind; namentlich kann die Täuschung gross werden, wenn der zweite oder der vierte, überhaupt die geradzahligen Teiltöne intensiv sind, da diese bekanntlich dem Grundtone ähnlicher klingen als die ungradzahligen Teiltöne. Natürlich können die letzteren auch zur Täuschung beitragen, indem sie den Eindruck des hohen Klanges verursachen. Wenn man aber die einzelnen Teiltöne des fraglichen Klangs irgendwie ausfindig machen kann, so ist die Aufgabe damit gelöst. Es ist aber nicht nötig alle Teiltöne zu untersuchen, sondern *man braucht ganz einfach zu untersuchen, ob der fragliche Klang den Ton 3 oder 5 enthält. Sind dieselben vorhanden, so ist der Klang qualitativ gleich* (1) *und im anderen Falle ist er gleich* (2), *so dass der Grundton zugleich mitbestimmt ist.* Nötigen Falls kann man sich noch von den höheren Teiltönen ungerader Ordnung Gebrauch machen.

Die Brauchbarkeit dieser Methode habe ich an einer Reihe von Klängen geprüft und bestätigt gefunden, indem ich die Klänge einfach durch das blosse Ohr analysirte. Im Folgenden teile ich nach Helmholtz[1] das practische Verfahren der Analyse mit, und füge Bemerkungen hinzu, welche ich für zweckmässig gefunhen habe.

[1] Helmholtz, l. c. S. 84.

Ist der Beobachter musikalisch, so hat er schon die zu untersuchenden Teiltöne im Kopfe, so dass er zur Analyse einfach den zu untersuchenden Klang laut genug anzuregen und aufmerksam zuzuhören braucht, ob der dritte oder der fünfte Teilton der Reihe (1), also der niederen der beiden fraglichen Reihen enthalten ist. Die Entscheidung geschieht also nur nach einigen Versuchen, vorausgesetzt, dass der Beobachter genügende Uebung in der Analyse des Klanges hat; denn, musikalisch sein und analysiren können sind zwei verschiedene Sachen, wie Helmholz hervorhebt.

Wenn dagegen der Beobachter nicht musikalisch ist, so muss er irgend ein Instrument zu Hülfe nehmen, um sich erst mit dem zu untersuchenden Teilton bekannt zu machen. Ein Klavier oder ein Phisharmonica ist dazu nicht ganz gut geeignet, wenn es sich um beliebege Töne handelt. Am geeignetesten fand ich ein Monochord mit Metallsaite in folgender Weise zu gebrauchen. Man spanne die Saite so lange auf, bis der Grundton derselben gleich dem Grundton 1 der niederen Reihe (1) wird. Im Falle dies mit der gegebenen Saite nicht erreichbar ist, soll man eine andere passende Saite aufsuchen. Der so erhaltene Grundton 1 ist gewöhnlich eindeutig, aber wenn derselbe ebenfalls unsicher ist, so kann das nach dem Th. Young'schen Satze[1] bestimmt werden, indem man die Mitte der Saite zupft oder streicht, wobei die täuschenden geradzahligen Teiltöne verschwinden.

Wenn somit 1 hergestellt ist, so ist unsere Aufgabe jetzt die, zu entscheiden, ob der fragliche Grundton x gleich 1 oder 2 ist. Man hat also jetzt zu untersuchen, ob der Klang den Teilton 3 d. h. die Duodecime von 1 enthält. Um nun 3 in Erinnerung zu bringen berühre man die Saite links an der Stelle $\frac{1}{3}$ der ganzen Saitenlänge mit einem nachgiebigen Stäbchen, wie Federkiel, welches man an der linken Hand hält, ganz leise und zupfe den rechten Teil der Saite ebenfalls leise, wobei der Flageoletton der Duodecime entsteht. Gleich darauf lasse man den fraglichen Klang laut genug ertönen und höre aufmerksam nach der Duodecime zu. Ist 3 darin enthalten, so ist sicher,

[1] Helmholtz, l. c. S. 89.

dass der fragliche Klang qualitativ durch die Reihe (1) dargestellt wird, so dass notwendig $x=1$ sein mass, Ist dagegen 3 nicht zu hören, so kann das eine zweifache Bedeutung haben, die Ungeübtheit des Beobachters natürlich ausgeschlossen. Erstens kann der Klang durch die Reihe (2) dargestellt werden, in welchem Falle $x=2$ sein muss. Oder zweitens kann der Ton 3 ausnahmsweise in dem Klang fehlen, selbst wenn er der Reihe (1) angehört. Um diese Unbestimmtheit zu entscheiden nehme man wieder das Monochord zu Hülfe und berühre die Saite an der Stelle $\frac{1}{5}$ der ganzen Länge, bringe den fünften Teilton d. h. die Terz der zweiten Octave des Grundtones 1 in Erinnerung und suche den nämlichen Ton in dem betrachteten Klange in genau derselben Weise wie vorher. Ist derselbe darin vorhanden, so ist sicher, dass $x=1$ ist. Im Falle weder der dritte noch der fünfte Teilton der Reihe (1) in dem Klange zu finden ist, kann man mit grosser Sicherheit behaupten, dass der Klang der Reihe (2) angehört, somit $x=2$ ist, denn es kommt äusserst selten vor, dass zwei solche Teiltöne gleichzeitig fehlen. Natürlich kann man auch zur Controlle die Untersuchung über die siebenten und neuten Teiltöne ausdehnen, welche in vielen Fällen noch deutlich genug sich wahrnehmen lassen. Es ist einen glücklichen Zufall zu nennen, dass die zu untersuchenden Teiltöne die ungeradzahligen sind, da diese bekanntlich viel leichter zu hören sind, als die geradzahligen.

Als Saite des Monochords ist ein Messingdraht vorzuziehen (ein dünner Stahldraht ist natürlich besser), weil derselbe gewöhnlich viel reicher an Obertönen sind, als eine Darmsaite oder eine Japanische Seidensaite. Anstatt die Saite durch Spanung auf den Grundton 1 zu stimmen, ist es natürlich bequemer einen beweglichen Steg zu Hülfe zu nehmen, aber ein Steg hat gewöhnlich eine eigentümliche abstumpfende Wirkung, so dass die Teiltöne weniger deutlich hervortreten. Auch scheint die Benutzung eines Steges daher nachteilich zu sein, weil der ausgeschlossene Teil der Saite an die Schwingung sich teilnimmt, was bei solchen sensitiven Beobachtungen störend wirken kann.

Bei der Erzeugung des Flageolettones hat man sich darauf zu achten, nicht etwa die Knote, sondern den Bauch der durch Berührung erzeugten Wellen zu zupfen, da im ersten Falle, wie schon erwähnt, nach Th. Young, gerade der gewünschte Ton ausgelöscht wird. Anstatt die Teilung der Saite mit einem Federkiel zu machen, kann man auch mit Vorteil von einer Reihe von Kunstgriffen Gebrauch machen, um schöne Flageolettöne hervorzubringen. Da man aber zu solchen Kunstgriffen von selber geführt wird, so sei hier nur einer beschrieben. Man falte ein Stuck steifes Papier und lege dasselbe mit der Kante auf den Teilpunkt der Saite, indem man das Papierstückchen zwischen zwei Fingern der linken Hand hält. Zupft man nun die Saite mit der rechten Hand, so erhebt sich das Papierstückchen durch die Erschütterung in die Höhe und bleibt durch Reibung zwischen den Fingern, und es entsteht ein recht sanfter Flageoletton. Anstatt des Flageolettones kann man natürlich auch den Ton selber anregen, indem man den linken Teil des Teilpunktes zupft. Dabei und überhaupt muss man beim Zupfen besonders vorsichtig sein, damit der Ton nicht zu stark erregt wird. Da nämlich die Teiltöne in dem fraglichen Klange nur schwach vertreten sein können, so darf der Ton, den man zur Erinnerung bringen will, nicht zu stark sein, damit derselbe möglichst ähnlich dem zu vergleichenden Teilton klingt, was ja die Hauptbedingung des Urteils ist.

Die Möglichkeit, dass man in dem Urteile der Teiltöne ebenfalls um eine Octave sich irrt, ist zwar nicht ausgeschlossen, aber es kommt wohl nicht vor, dass man in dem Urteile aller Teiltöne unsicher bleibt; die Eindrücke verschiedener Teiltöne unterstützen sich nämlich gegenseitig, um das richtige Urteil zu geben.

Demjenigen, welcher die Analyse des Klanges durch das blosse Ohr zum ersten Male versucht, kann diese Methode im ersten Blicke recht schwer auffallen, selbst für ein sonst sehr geübtes Ohr. In diesem Falle ist es ratsam, erst einige Vorübungen mit Metalldrähten zu machen und dann zur eigentlichen Analyse des fraglichen Klanges zu übergehen. Wenn man bei der Vorübung einmal einen Teilton herausgefunden hat und ist man in den

Ton vertieft, so kommt es einem vor, als ob nur dieser Ton aber keine andere Töne vorhanden wären und unwillkürlich frägt man sich, wie war es denn möglich, dass Du vorher diesen Ton nicht hören konntest? Hat man sich in der Analyse so weit geübt, so ist die Lösung der Aufgabe nunmehr eine Leichtigkeit.

Bei den Klängen, welche nicht aus den harmonischen Teiltönen zusammengesetzt sind, müssen die individuellen Teiltöne anderweitig bekannt sein, um die Methode anwenden zu können. Bei der Stimmgabel wissen wir z. B., dass die Teiltöne bei dem Grundtone *c* die folgenden sind:

$$c,\ gis_2,\ fis_3,\ d_4,\ gis_4,\ cis_5 + \ldots\ldots\ldots$$

Die Obertöne scheinen mir mit den Stimmgabeln einwenig zu schwanken, aber dieser Umstand stört die Anwendung unserer Methode nicht, da es nur darauf ankommt zu entscheiden in welcher Octave der zu suchende Teilton enthalten ist.

Short Period Magnetographs.

By

Yoshisaburô Kashiwagi.

---

1. In the present paper I shall give an account of some preliminary experiments performed with magnetic intensity variometers of my own design. It is a long time since the author intended to obtain a variometer for recording magnetic disturbances of short duration occuring at short intervals, and also, if possible, recording magnetic variations of longer periods. For this purpose, the instrument should be quickly as well as faithfully responsive to instantaneous value of magnetic force, so that the movable part of the instrument must be free from any friction, and its own period of oscillation sufficiently small, as well as that the oscillation be highly damped.

2. Now, the period may be made small in two different ways: (1) by diminishing the moment of inertia of the movable part; and (2) by increasing the moment of force acting upon the latter.

The decrease of the moment of inertia is, however, generally accompanied by a decrease of the moment of force. Thus, with a magnet oscillating about an axis perpendicular to its length, the period is, at least:

$$T_1 = L\sqrt{\frac{\rho \text{ arc } 1'}{12\, I s}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1),$$

where L is the length of the magnet; ρ its density; I its intensity of magnetization; and s the sensibility, i. e., the amount of field variation producing deflection $1'$ of the magnet statically. Hence, the period T_1 may be made smaller, without loss of sensibility, by making L smaller; but it has a certain limit, because in the

case of a small magnet, the effect of the moment of inertia of appendages such as the suspension frame and the mirror becomes considerable.

Of the variometers with small periods used by different authors, Eschenhagen's[1] seems to have the smallest period of about 4·25 sec. for the sensibility of 0·3 γ. This will be the smallest period attainable by simply diminishing the moment of inertia of the needle; because if we apply the above-mentioned formula, for example, $\rho=7{\cdot}8$, $I=200$, $s=0{\cdot}30\times10^{-5}$ and $L=2$, we obtain $T_1=4{\cdot}26$.

Thus, in order to make the period smaller, we have to appeal to the second way. The moment of force acting upon the suspended magnet depends firstly upon the magnetic moment of the magnet, and secondly, upon the magnetic force acting upon it. So far as the intensity of magnetization remains constant, an increase of the magnetic moment will be accompanied by an increase of period. To increase the magnetic force, we have no other recourse than to make use of a paramagnetic substance.

Luckily enough, as to the quick and faithful responsibility of iron to a variation of magnetic force, in 1887 Lord Rayleigh[2] established experimentally that the change of induced magnetism is proportional to the change of magnetizing force, when that change is very small.

Under these circumstances, the author devised new forms of variometers which may have smaller periods and are applicable to variations in any desired direction. These instruments are nothing more than modifications of Lloyd's variometer. Unlike the latter, however, in these modified forms, the deflections become quite free from variations of components not in the desired direction.

3. Let us first describe the principle of the author's instrument used for the measurement of the vertical component:

The essential points of the modification consist in that an

[1] Sitzungsber. d. Berl. Akad. d. Wiss. 1896, s. 966.

[2] Phil. Mag. vol. 23, p. 225, 1887.

astatic system of magnets is taken instead of a single needle, and three iron bars instead of two. The arrangement is as shown in the annexed figure. *AB*, *CD* and *EF*, are iron bars attached to the surface of a copper tube along the two diametrically opposite lines. The bars, together with the tube, can be kept in vertical position by means of levelling screws.

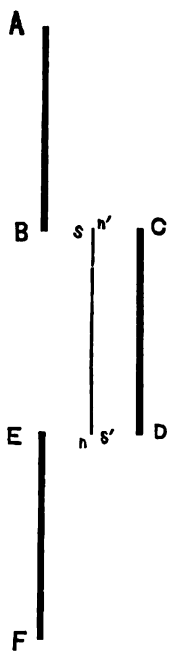


FIG. 1.

At the middle of the tube, an astatic system, consisting of two vertical magnets *n s* and *s' n'*, is suspended symmetrically with respect to *B*, *C*, *E*, and *D*, with its axial plane *n s n' s'* perpendicular to the plane of the inducing bars.

The effect of induction due to the horizontal component of the terrestrial magnetic field cancels itself on account of the symmetry of the construction. The vertical component induces at *A*, *C*, and *E*, the south, and at *B*, *D*, and *F*, the north-seeking poles in a region of north inclination. Thus the magnetic force at the middle of *B* and *C* acts from *B* to *C*, while at the middle of *E* and *D*, from *D* to *E*, so that they co-operate to turn the astatic system in the same direction; and this resultant couple is equilibrated by the torsion of the suspension system. In this state, any further changes of the vertical intensity will cause a deflection of the astatic system.

Now, the field intensity between the pairs of the induced poles is not uniform, but it varies continuously from point to point. The deflection of the astatic system will, therefore, be proportional to the variation of the vertical intensity so far as both are small.

With my arrangement, the adjustment of the instrument is independent of its orientation in azimuth; while the balance type

variometer is liable to shift in the horizontal plane, in consequence of variations of declination. When the inducing bars are exactly in vertical position, any rotation of the whole instrument about a vertical axis will not affect the position of the astatic needles relative to the instrument, as the relation of all parts to the vertical intensity remains unchanged. Furthermore, we may utilize this for correcting the verticality of the inducing bars, and this having been done once for all, we may afterwards simply rely upon sensitive levels attached to the instrument.

4. Next, for the measurement of the variations of horizontal component, or component in any inclined direction: two pairs of iron bars, other things remaining as before, are employed instead of the three vertical ones. Their arrangement is shown in Fig. 2. The heavy lines represent the bars. The inner pairs of induced poles of the bars are at the same level as the poles of the astatic needles with their lengths in the required direction, the line joining the said induced poles being perpendicular to the bars. When the symmetry of the arrangement is perfect, the indication of the instrument will always be independent of the components of the field perpendicular to the direction of the bars.

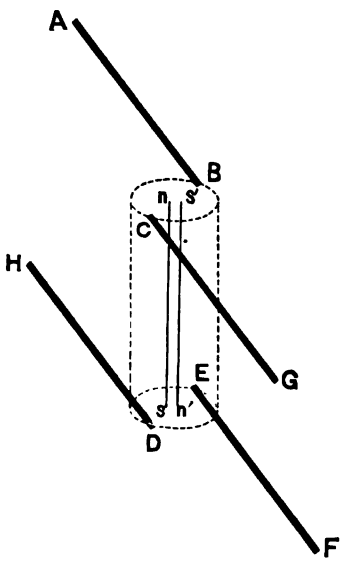


FIG. 2.

5. The relation between the periods of oscillation and the sensibility of the above mentioned instruments, may be calculated approximately as follows:

Let the cross sections of the inducing bars and the lateral dimensions of the astatic system be small compared with BC or DE. Then the field intensity at the middle of B and C or D and E is

$$\frac{2kFA}{r^2},$$

where k is the susceptibility, A the sectional area of each of the inducing bars, $r=\frac{BC}{2}=\frac{DE}{2}$, and F the component of the earth field in the direction of the bars. If the magnetic moment of a pair of poles of an astatic system, ns' or $n's$ be M, then the resultant couple acting upon the astatic system will be

$$\frac{4kFAM}{r^2}.$$

Let this couple be equilibrated by turning the torsion head through an angle φ, then, when the suspension is unifilar,

$$\frac{4kFAM}{r^2}=K_1\varphi \quad\text{.....(2)},$$

K_1 being a constant depending upon the suspension fibre; and when the suspension is bifilar,

$$\frac{4kFAM}{r^2}=K_2\sin\varphi \quad\text{.....(3)},$$

K_2 being the bifilar constant.

The variation $\Delta\varphi$ of the angle of torsion due to the variation ΔF of the field intensity in the above two cases is respectively given by

$$\Delta\varphi=\frac{4k'AM\Delta F}{r^2K_1} \quad\text{.....(4)},$$

and

$$\Delta\varphi=\frac{4k'AM\Delta F}{r^2K_2\cos\varphi} \quad\text{.....(5)},$$

where k' is the susceptibility corresponding to small variation of the field.

Thus the period of oscillation of the astatic system is

$$T_2=\pi\sqrt{\frac{N \text{ arc } 1'}{s\,\frac{4\,k'AM}{r^2}}} \quad \text{.....(6)},$$

where N is the moment of inertia of the suspended system, and s the sensibility of the instrument. When lateral dimensions of the suspended magnets are very small, and the moment of inertia of the appendage is neglected, the above expression may be transformed into

$$T_2=\pi L'\sqrt{\frac{\rho \text{ arc } 1'\, r^2}{8\, I s k' A p}} \quad \text{.....(7)},$$

where L' is the length of the suspended magnets, and $p=\frac{L'}{d}$, d being the horizontal distance between the poles of the astatic system, i. e. $n\,s'$ or $n'\,s$ in Fig. 2.

Comparing (1) and (7), we have, for equal sensibility,

$$\frac{T_2}{T_1}=\frac{L'}{L}\sqrt{\frac{3\,r^2}{2\,k'\,p\,A}} \quad \text{.....(8)}.$$

If we put $k'=6{\cdot}4$, which is the smallest value of susceptibility as obtained by Lord Rayleigh,[1] $r=0{\cdot}5$, $p=20$, and $A=0{\cdot}04$, for example, then

$$\sqrt{\frac{3\,r^2}{2\,k'\,p\,A}}=0{\cdot}27.$$

Thus, taking $L'=2$, we obtain $T_2=1{\cdot}15$, instead of $T_1=4{\cdot}26$ for the same sensibility as in the example given before; but we must not lay too much weight upon this value, as the effect of the neglected moment of inertia of the appendage becomes more considerable in the case of the astatic needles.

6. Now, the instrument constructed for the measurement of the vertical intensity variation is shown in Fig. 3.

The dimensions of the inducing bars are, each, 42 mm. × 6 mm. × 2 mm., and they are arranged not exactly as in Fig. 2, but

[1] Loc. cit.

Parts of the cover are taken away to show the interior.

A, B and **C** .....inducing bars.

D.....copper tube.

E and **F**.....astatic magnets.

M.....mirror attached to the astatic system.

M′.....fixed mirror.

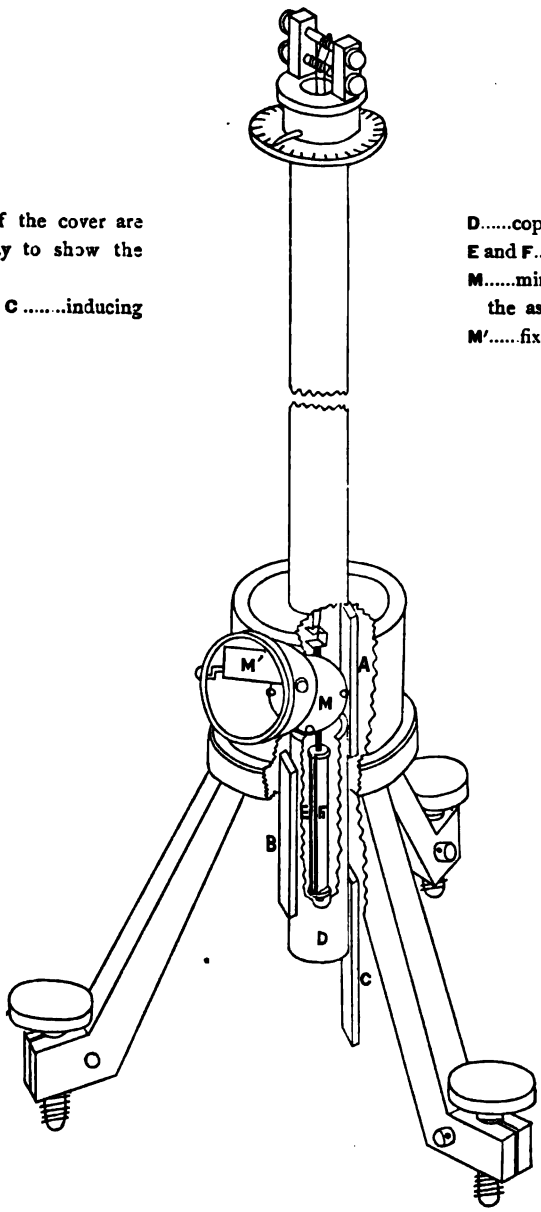


FIG. 3.

are made to overlap each other through a length of 4 mm. The external diameter of the copper tube carrying the iron bars measures 15·6 mm. The astatic system consists of a pair of magnets, each 40 mm. × 5 mm. × 1 mm. in dimensions, kept parallel to one another, at a distance of 1 mm., by means of a copper frame. The centering of the suspended system is determined by looking through a pair of openings cut in the wall of the copper tube. The torsional couple is applied by means of a bifilar suspension.

The instrument was set upon a brick pier in an underground chamber of this physical laboratory, where the diurnal variation of temperature is less than 1° C. This place was formerly a boiler-room, and its surroundings are not free from magnetic substances; but the author carried out the preliminary experiments there as there is not, at present, any other room available in which the temperature is constant.

Another instrument for a horizontal $N-S$ component variometer was also set up in the same chamber together with a Mascart's bifilar variometer. Each of the inducing bars of the above horizontal variometer consists of a bundle of 8 pieces of iron wires 1·5 mm. in diameter and 6 cm. in length. The astatic system of the latter is a little greater than that of the vertical variometer, the magnetic needles being each 50 mm. × 5 mm. × 1 mm. in dimensions, and their mutual distance being 2 mm.

All the observations were performed photographically. The field variation necessary for the measurement of sensibility was produced by passing a known electric current through a system of two equal coaxial flat coils of mean radius 14·48 cm., kept apart at a distance equal to the radius, and placed coaxially as well as symmetrically with respect to the system of inducing bars.

As to the suspension of the astatic system, on account of humidity we cannot make use of silk fibre, when the instrument is intended to record variations of longer period. Therefore the author used a fine copper wire, 0·0208 mm. in diameter, and it proved satisfactory.

7. It is now important to notice that when the temperature rises, magnetic moment of a magnet decreases, while susceptibility of iron increases. But the absolute amounts of these temperature coefficients are of the same order of magnitude, and in fact, in some specimens they are nearly equal. Hence, by proper choice of materials, it seems to be possible to make the effect of these variations cancel each other. The variation of the bifilar constant due to temperature is very small compared with either of the above variations.

The instruments employed by the author were, however, constructed with no special choice of materials. Thus it is desirable to determine experimentally the order of magnitude of the temperature coefficient of the instrument. In order to determine this temperature coefficient, the instrument was covered with a cylindrical zinc case surrounded with a coil of lead pipe through which hot or cold water was passed.

8. The results of the preliminary observations are collected under the following heads:

(i) Proportionality of the variations of field intensity produced statically and the consequent deflections.

This was verified for a range of $\pm 50\gamma$.

(ii) Relation between the period of oscillation and the sensibility.

The observed period was:

2·0 sec. for $s=2{\cdot}6\gamma$ for the horizontal intensity variometer, and 3·0 sec. for $s=1{\cdot}9\gamma$ and 1·4 sec. for $s=7{\cdot}9\gamma$ for the vertical intensity variometer.

In the last case the period calculated from the formula (6) is 1·2 sec., when we put $k'=6{\cdot}4$, $A=0{\cdot}12$, $r=0{\cdot}88$, $N=0{\cdot}28$, and $M=1{\cdot}76$. These values for N and M were calculated from the dimensions of the suspended system and the magnetic moments of the separate needles.

It must be remarked that the above values of periods are not the limiting ones attainable with a variometer of the author's type. They can be, of course, made much smaller by improving the instruments.

(iii) Damping.

The damping ratios of the vertical and the horizontal intensity variometers were respectively about 1·05 and 1·07 per second, for sensibilities ranging from 2γ to 8γ. The damping may be increased at will, if required.

(iv) Temperature coefficient.

This was determined for the vertical intensity variometer only. When the temperature was raised, the mirror deflected to the side corresponding to the decrease of the field. The mean temperature coefficient between 12° and 24° was about 25γ per 1° C., which is a little less than that of Mascart's balance at our Central Meteorological Observatory in Tôkyô.[1]

(v) Applicability of the instruments to variations of longer periods.

The photographic records for the vertical intensity taken throughout a whole day fairly coincided with those given by the balance type variometer at Kamigamo, distant about 4·3 km. from our laboratory. The only difference observed is that our records have zigzag curves during the working hours of the electric trams in the city, while the Kamigamo records are quite free from such disturbances. The nearest one of the trams is distant about 1 km. from our laboratory: the system is a single trolley one, and the rails are not insulated from the ground.

With regard to the records taken on the same paper with two other variometers, set up in the underground chamber, we see that they coincide with one another, on the whole, but the portions corresponding to the disturbances due to the electric trams showed a marked difference, owing to the difference of periods and dampings.

A few of these records are reproduced in Fig. 4, annexed at the end of this article.

(vi) Constancy of the instruments.

The horizontal intensity variometer used by the author was

[1] Annual Report of the Centr. Meterorolog. Observatory of Japan for 1901, Part II, No. 2, p. 5. 1906.

constructed for temporary use and contained loosely connected parts. It showed a gradual change of zero position, so that it ought to be readjusted after a few days. The vertical variometer showed no considerable change of zero position, but the amount of this change was not ascertained. Hence the author is not able to say whether these instruments will show any irregularity in the course of months on account of certain causes, such as hysteresis of iron. The author hopes to determine these points by future research to be carried through a longer interval with instruments constructed rigid enough and of materials specially chosen.

Physical Laboratory,
January 1907.

On the Theory of the Rotary Converter.

By

Tarô Ôtake.

In the ordinary theory of the rotary converter, it is taken for granted that the direct and the alternating current sides are independent of each other, so that the whole may be seen as a combination of a synchronous motor and a direct current generator; but if this assumption is not taken, the solution of the problem may reveal a different aspect.

My present purpose is to study the properties of the rotary converter from this different standpoint and, if possible, to account for some experimental results already obtained, which seem not to have had proper explanation in the ordinary theory.

But, as is well known, when we are treating of problems in which such things as armature reaction, hysteresis, fluctuation of lines of force, etc., play the important part, it is usual for the analysis to give a result which, though complicated, does not fall very closely in with the actual facts.

Therefore, the following conclusions, even though there may be no blunder committed in the deductions, are to be taken only as vaguely indicating the actual state of things.

Here, the discussion relates to the uniarmature synchronous rotary converter and, for the sake of simplicity, a bipolar case is considered, as a multipolar case may be considered as an aggregate of bipolar cases: consequently, the results deduced in the latter case may be applied to the former without much modification.

The exposition is to take the following orders:—

A. Direct current side:

a. 1. The case of an odd number of phases,
2. Examination of the values of e's,
3. Calculation of necessary constants.

b. 1. The case of an even number of phases,
2. Calculation of necessary constants.

c. Solution of the equations obtained in cases *a.* and *b.*

B. Alternating current side:

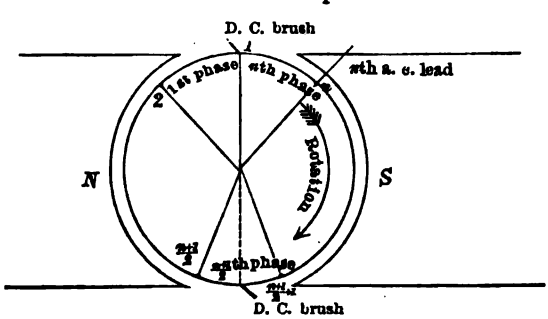
d. Currents in all phases.

e. Currents in all leads.

C. Inferences drawn from the results obtained in A and B.

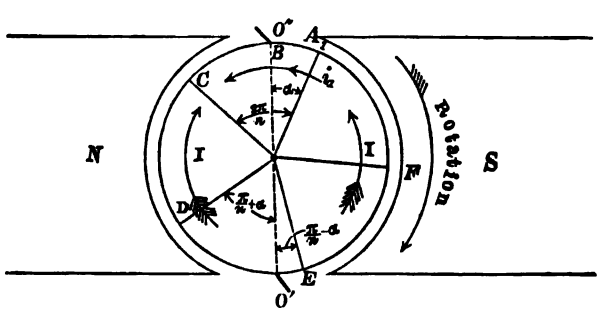
The rotary converter may be shown diagrammatically as follows:
In the case of an odd number of phases:

FIG. 1.



A. *a.* 1. In the case of an odd number of phases:

FIG. 2.



Now, suppose the point I has traveled through an angle α from the position in Fig. 1.

Let $a=\dfrac{\alpha}{\frac{2\pi}{n}}$,

r=resistance per phase,

L=coefficient of self induction of conductors per phase, due to the flux interlinking the conductors only

e_r=induced E. M. F. of rth phase at the position shown in Fig. 2 caused by the flux started by the field coils and the armature reaction.

$$E_1 \sin\left(wt+\beta-\frac{2\pi(r-1)}{n}-\frac{\pi}{n}\right)+E_3 \sin 3\left(wt-\frac{2\pi(r-1)}{n}-\frac{\pi}{n}\right)$$

$+F_3\cos 3\left(wt-\dfrac{2\pi(r-1)}{n}-\dfrac{\pi}{n}\right)+\cdots\cdots$ applied voltage at rth and $r+1$th terminals counting the time from the position of the point 1 at O',

$2I$=current taken out to the direct current side.

$i\pm I$ current in the rth phase, where $\pm$ sign is to be taken according as the rth phase is or is not at the right-hand side $O'O''$.

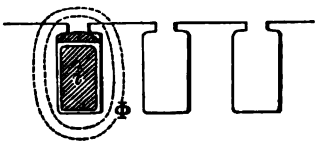
It should be remarked that i is used only to signify the difference between the actually flowing current (in the direction ←■) and I.

I. Then as long as $\alpha<\frac{1}{2}\left(\frac{2\pi}{n}\right)$ or $a<\frac{1}{2}$ the following relations exist, taking the direction of i as shown in Fig. 2, and assuming that the E. M. F. e_r takes the opposite direction to the current.

The resistance between A and B is equal to ra, and the coefficient of self induction between A and B is equal to La.

Of these two, the former is evident; the latter can be shown as the following.

Since this is chiefly due to the flux Φ's interlinking the slots or conductors, as the following figure shows,



it may be expressed as

$$L \cong \frac{mc\Phi}{i},$$

where i=current in the conductor,

m=total number of the slots per phase,

c=the number of conductors in a slot (supposed to be all in series).

The number of slots contained between A and B is $\sim m.\,a$, therefore, the above stated result follows.

Similarly as to BC,

resistance of $BC = r(1-a)$,

coefficient of self induction of $BC = L(1-a)$.

Therefore, for the circuit AC, assuming that the commutation takes place in a very short time,

$$L\frac{d}{dt}\{(I+i_1)a\} + (I+i_1)ar + L\frac{d}{dt}\{(i_1-I)(1-a)\} + (i_1-I)(1-a)r$$
$$+ e_1 = E_1\sin\left(wt+\beta-\frac{\pi}{n}\right) + \cdots\cdots\cdots$$

rearranging

$$L\frac{d}{dt}\{(2a-1)I\} + (2a-1)Ir + L\frac{di_1}{dt} + i_1r + e_1 = E_1\sin\left(wt+\beta-\frac{\pi}{n}\right) + \cdots\cdots$$

Similarly as to $O'E$,

resistance of $O'E = r(\frac{1}{2}-a)$,

coefficient of self induction of $O'E = L(\frac{1}{2}-a)$,

and as to $O'D$,

resistance of $O'D = r(\frac{1}{2}+a)$,

coefficient of self induction of $O'D = L(\frac{1}{2}+a)$.

$$\therefore\quad L\frac{d}{dt}\{(I+i_{\frac{n+1}{2}})(\tfrac{1}{2}-a)\} + (I+i_{\frac{n+1}{2}})(\tfrac{1}{2}-a)r + L\frac{d}{dt}\{(i_{\frac{n+1}{2}}-I)(\tfrac{1}{2}+a)\}$$
$$+ (i_{\frac{n+1}{2}}-I)(\tfrac{1}{2}+a)r + e_{\frac{n+1}{2}} = E_1\sin\left\{wt+\beta-\frac{2\pi}{n}\left(\frac{n-1}{2}\right)-\frac{\pi}{n}\right\} + \cdots\cdots$$

i. e.

$$-L\frac{d}{dt}(2aI)-2aIr+L\frac{di_{\frac{n+1}{2}}}{dt}+i_{\frac{n+1}{2}}r+e_{\frac{n+1}{2}}$$
$$=E_1\sin\left\{wt+\beta-\frac{2\pi}{n}\left(\frac{n-1}{2}\right)-\frac{\pi}{n}\right\}+\cdots\cdots\cdots\cdots\cdots\cdots$$

For the 2nd phase

$$L\frac{d}{dt}(i_2-I)+(i_2-I)r+e_2=E_1\sin\left(wt+\beta-\frac{2\pi}{n}-\frac{\pi}{n}\right)+\cdots\cdots\cdots$$

The similar expressions hold for other phases.

At $a=\frac{1}{2}\left(\frac{2\pi}{n}\right)$ or $a=\frac{1}{2}$ the point E coincides to one brush practically, though strictly considered there lies a conductor having resistance, coefficient of self induction and counter E. M. F. between the point E and the brush.

II. If E passes over O', making any angle a i. e. $a\cdot\frac{2\pi}{n}$ with the brush line, we have

$$L\frac{d}{dt}(2aI)+2aIr+L\frac{di_1}{dt}+i_1r+e'_1=E_1\sin\left(wt'+\beta-\frac{\pi}{n}\right)+\cdots\cdots\cdots,$$

and $$L\frac{d}{dt}\{(1-2a)I)+(1-2a)Ir+L\frac{di_{\frac{n+1}{2}+1}}{dt}+i_{\frac{n+1}{2}+1}r+e'_{\frac{n+1}{2}+1}$$
$$=E_1\sin\left\{wt'+\beta-\frac{2\pi}{n}\left(\frac{n+1}{2}\right)-\frac{\pi}{n}\right\}+\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots,$$

since EF, AC are in positions similar to those of AC, DE in the previous case respectively.

Other phases take the same equations as in the former case, if e'_r's, wt' be put for e_r's, wt.

At $a=1$, the armature has traveled through an angle $\frac{2\pi}{n}$, and all conditions are quite the same as the initial instant $a=0$.

Therefore, the above stated two states are successively repeated and consequently the examination of these two cases will suffice for our purpose.

Summarizing the results above deduced, we have:

I. Putting $\varphi = wt + \beta - \frac{\pi}{n}$,

$$
(\mathrm{I})\begin{cases}
L\frac{d}{dt}\{(2a-1)I\} + (2a-1)I_r + L\frac{di_1}{dt} + i_1 r + e_1 = E_1 \sin\varphi + \cdots\cdots (I_1), \\
-\left(L\frac{dI}{dt} + Ir\right) + L\frac{di_2}{dt} + i_2 r + e_2 = E_1 \sin\left(\varphi - \frac{2\pi}{n}\right) + \cdots\cdots\cdots\cdots (I_2), \\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
\pm\left(L\frac{dI}{dt} + Ir\right) + L\frac{di_r}{dt} + i_r r + e_r = E_1 \sin\left(\varphi - \frac{2\pi}{n}(r-1)\right) + \cdots\cdots (I_r), \\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
-\left(L\frac{d(2aI)}{dt} + 2aIr\right) + L\frac{di_{\frac{n+1}{2}}}{dt} + i_{\frac{n+1}{2}} r + e_{\frac{n+1}{2}} \\
\qquad = E_1 \sin\left\{\varphi - \frac{2\pi}{n}\left(\frac{n-1}{2}\right)\right\} + \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (I_{\frac{n+1}{2}}).
\end{cases}
$$

II. Putting $\varphi' = wt' + \beta - \frac{\pi}{n}$,

$$
(\mathrm{II})\begin{cases}
L\frac{d}{dt}(2aI) + 2aIr + L\frac{di_1}{dt} + i_1 r + e'_1 = E_1 \sin\varphi' + \cdots\cdots\cdots\cdots\cdots (II_1), \\
-\left(L\frac{dI}{dt} + Ir\right) + L\frac{di_2}{dt} + i_2 r + e'_2 = E_1 \sin\left(\varphi' - \frac{2\pi}{n}\right) + \cdots\cdots\cdots (II_2), \\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
\pm\left(L\frac{dI}{dt} + Ir\right) + L\frac{di_r}{dt} + i_r r + e'_r = E_1 \sin\left(\varphi' - \frac{2\pi}{n}(r-1)\right) + \cdots\cdots (II_r), \\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
L\frac{d}{dt}\{(1-2a)I) + (1-2a)Ir + L\frac{di_{\frac{n+1}{2}+1}}{dt} + i_{\frac{n+1}{2}+1} r + e'_{\frac{n+1}{2}+1} \\
\qquad = E_1 \sin\left\{\varphi' - \frac{2\pi}{n}\left(\frac{n+1}{2}\right)\right\} + \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (II_{\frac{n+1}{2}}).
\end{cases}
$$

Let the direct current side have a counter E. M. F., C (supposed to be constant), resistance R_e and a coefficient of self induction L_e. Then, as Fig. 3 shows

FIG. 3.

resistance between $OGB = \frac{nr}{2}$,

coefficient of self induction between $OGB = \frac{nL}{2}$,

and for the case I,

$$\left(\frac{nL}{2}+2L_e\right)\frac{dI}{dt}+\left(\frac{nr}{2}+2R_e\right)I-\left(L(1-a)\frac{di_1}{dt}+(1-a)i_1r+L\frac{di_2}{dt}+i_2r\right.$$

$$\left.+\cdots+L\frac{di_r}{dt}+i_rr+\cdots+L(\tfrac{1}{2}+a)\frac{di_{\frac{n+1}{2}}}{dt}+(\tfrac{1}{2}+a)i_{\frac{n+1}{2}}r\right)=e_0-c\ldots\text{(III)}.$$

For the case II, taking $BG'O$,

$$\left(\frac{nL}{2}+2L_e\right)\frac{dI}{dt}+\left(\frac{nr}{2}+2R_e\right)I+\left(L(\tfrac{1}{2}+a)\frac{di_1}{dt}+(\tfrac{1}{2}+a)i_1r+L\frac{di_n}{dt}+i_nr\right.$$

$$\left.+\cdots+L\frac{di_r}{dt}+i_rr+\cdots+L(1-a)\frac{di_{\frac{n+1}{2}+1}}{dt}+(1-a)i_{\frac{n+1}{2}+1}r\right)=e_0-c\ldots\text{(IV)},$$

where e_0 signifies the E. M. F. induced among BGO or $BG'O$ in the direction of I.

Now, making the operation, $(I_1)\cdot(1-a)+\sum_{2}^{\frac{n-1}{2}}r(I_r)+(I_{n+1})(\tfrac{1}{2}+a)$ $+$(III) we have

$$\left(\frac{3}{2}L+2L_e\right)\frac{dI}{dt}+\left(\frac{3r}{2}+2R_e\right)I+(1-a)\left(L\frac{d\{(2a-1)I\}}{dt}+(2a-1)Ir\right)$$

$$-(\tfrac{1}{2}+a)\left(L\frac{d}{dt}(2aI)+2aIr\right)+c-e_0+e_1(1-a)+e_2+\cdots\cdots\cdots\cdots$$

$$+e_{\frac{n-1}{2}}+(\tfrac{1}{2}+a)e_{\frac{n+1}{2}}=(1-a)(E_1\sin\varphi+\cdots)+\left\{E_1\sin\left(\varphi-\frac{2\pi}{n}\right)+\cdots\right\}$$
$$+\cdots\cdots+\left\{E_1\sin\left[\varphi-\frac{2\pi}{n}\left(\frac{n-1}{2}-1\right)\right]+\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\right\}$$
$$+(\tfrac{1}{2}+a)\left\{E_1\sin\left[\varphi-\frac{2\pi}{n}\left(\frac{n-1}{2}\right)\right]+\cdots\cdots\right\}\cdots\cdots\cdots\cdots\cdots\cdots\cdots(\mathrm{V}_a).$$

Putting, now,

$$\frac{3}{2}L+2L_e=\lambda,\qquad \frac{3}{2}r+2R_e=\rho,$$
$$e_1(1-a)+e_2+\cdots\cdots+e_{\frac{n-1}{2}}+(\tfrac{1}{2}+a)e_{\frac{n+1}{2}}=\Sigma e,$$
$$(1-a)(E_1\sin\varphi+\cdots\cdots)+\left\{E_1\sin\left(\varphi-\frac{2\pi}{n}\right)+\cdots\cdots\right\}+\cdots\cdots\cdots\cdots\cdots\cdots$$
$$\cdots\cdots\cdots+\left\{E_1\sin\left[\varphi-\frac{2\pi}{n}\left(\frac{n-1}{2}-1\right)\right]+\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\right.$$
$$\left.\cdots\cdots\cdots\right\}+(\tfrac{1}{2}+a)\left\{E_1\sin\left[\varphi-\frac{2\pi}{n}\left(\frac{n-1}{2}\right)\right]+\cdots\cdots\cdots\cdots\cdots\cdots\cdots\right\}=\Sigma E,$$

and $$\frac{d}{dt}L(a-1)=L\cdot\frac{\omega}{\frac{2\pi}{n}}=Lk,$$

(V_a) becomes

$$\lambda\frac{di}{dt}+\rho I+\left(L\frac{dI}{dt}+Ir\right)(2a-1-4a^2)-LkI(4a-1)+\Sigma e-e_0+c$$
$$=\Sigma E\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(\mathrm{V}_b).$$

Similarly making

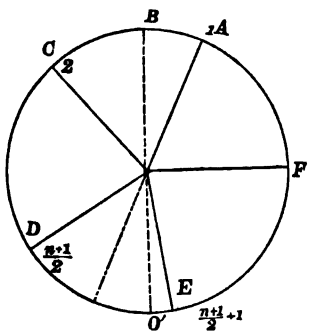
$(\mathrm{II}_1)(\tfrac{1}{2}+a)+\sum\limits_{\frac{n+1}{2}+2}^{n}r(II_r)+(II_{\frac{n+1}{2}+1})(1-a)-(IV)$, we have

$$-(\tfrac{3}{2}L+2L_e)\frac{dI}{dt}-(\tfrac{3}{2}r+2R_e)I+(\tfrac{1}{2}+a)\left(L\frac{d}{dt}(2aI)+2aIr\right)$$
$$+(1-a)\left(L\frac{d}{dt}[(1-2a)I]+(1-2a)Ir\right)+e_0-c+e'_1(\tfrac{1}{2}+a)+e'_n$$
$$+e'_{n-1}+\cdots\cdots+e'_{\frac{n+1}{2}+2}+e'_{\frac{n+1}{2}+1}(1-a)=(\tfrac{1}{2}-a)(E_1\sin\varphi'+\cdots\cdots)$$
$$+\left\{E_1\sin\left(\varphi'-\frac{2\pi}{n}(n-1)\right)+\cdots\cdots\right\}+\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$
$$+(1-a)\left\{E_1\sin\left[\varphi'-\frac{2\pi}{n}\left(\frac{n+1}{2}\right)\right]+\cdots\cdots\right\}\cdots\cdots\cdots\cdots\cdots(\mathrm{VI}_a).$$

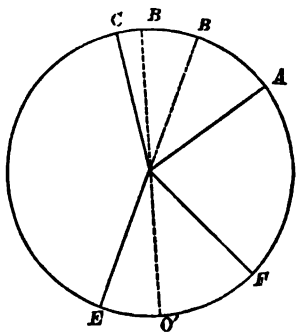
i. e.

$$-\lambda\frac{dI}{dt}-\rho I-\left(L\frac{dI}{dt}+Ir\right)(2a-1-4a^2)+LkI(4a-1)+\Sigma e'+e_0-c$$
$$=\Sigma E' \quad\text{.....}(\mathrm{VI}_b).$$

Moreover, from the diagrams of the cases I and II



CASE I.



CASE II.

it follows that

$$\left.\begin{array}{l} e_1=-e'_{\frac{n+1}{2}+1}, \\ e_2=-e'_{\frac{n+1}{2}+2}, \\ \dots\dots\dots\dots \\ e_{\frac{n+1}{2}}=-e'_1, \end{array}\right\}$$

for $0<a<\frac{1}{2}$.

Also similar relations hold for $(E\sin\varphi+\cdots\cdots)$, ..., $\left\{E_1\sin\left[\varphi-\frac{2\pi}{n}\left(\frac{n-1}{2}\right)\right]+\cdots\cdots\right\}$, and $(E_1\sin\varphi'+\cdots\cdots)$, ..., $\left\{E_1\sin\left[\varphi'-\frac{2\pi}{n}\left(\frac{n+1}{2}\right)\right]+\cdots\cdots\right\}$.

Therefore (V_b), (VI_b) are convertible into an equation:

$$\lambda\frac{dI}{dt}+\rho I+\left(L\frac{dI}{dt}+Ir\right)(2a-1-4a^2)-LkI(4a-1)=e_0-c+\Sigma E-\Sigma e.$$

This equation, when solved, gives the value of I, but the strict solution of this equation, even when worked out thoroughly,

seems to be too complicated to use or to draw any conclusion from it.

Since Lk and r are not large, we may, without any great error, take instead of $(2a-1-4a^2)$ and $(4a-1)$, their mean values, i. e. $-\frac{5}{6}$ and 0.

Then putting $\lambda-\frac{5}{6}L=\lambda_1$, $\rho-\frac{5}{6}r=\rho_1$,

we have $\lambda_1\frac{dI}{dt}+I\rho_1=e_0-c+\Sigma E-\Sigma e$.....(VII).

As has been already mentioned, this relation exists during the rotation of the armature through an angle $\frac{2\pi}{n}$ and is successively repeated. Therefore, we may consider that $\Sigma E-\Sigma e$ is a periodic function with a period of $2n$ times that of the E. M. F's. induced or voltage applied.

Hence, by applying Fourier's series, we shall decompose it into harmonics of periods of $2nm$ times that of the E. M. F. ($m=1$, 2, 3.....), and for this purpose, in the first place, it must be examined to determine what expressions the e's assume.

A. *a.* 2. Examination of Values of e's.

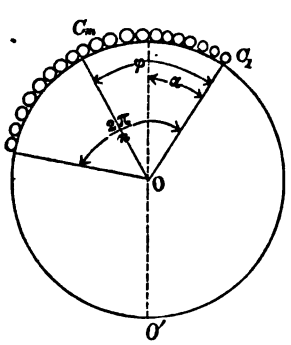


FIG. 4.

Let $c_1, c_2, \ldots\ldots c_s$ be the conductors of the first phase (many conductors in one slot are supposed to be concentrated into one conductor), then calculating the time from the instant at which the conductor c occupies O', the E. M. F. induced in c_m (Fig. 4) may be expressed as

$$e_m=A_1\sin(\pi+\alpha+\varepsilon-\varphi)$$
$$+A_3\sin 3(\pi+\alpha-\varphi)+\cdots\cdots$$
$$+B_3\cos(\pi+\alpha-\varphi)+\cdots\cdots,$$

where ε=angle between the brush and the neutral.

Therefore, the total E. M. F. in the 1st phase is

$$e_1=\Sigma e_m=\frac{m}{2\pi}\int_0^{\frac{2\pi}{n}} e_m d\varphi,$$

where m is the total number of the conductors.

$$e_1=\frac{m}{\pi}\left\{A_1\sin\frac{\pi}{n}\sin\left(\pi+\alpha+\varepsilon-\frac{\pi}{n}\right)+\frac{A_3}{3}\sin\frac{3\pi}{n}\sin 3\left(\pi+\alpha-\frac{\pi}{n}\right)+\cdots\cdots\right.$$
$$\left.+\frac{B_3}{3}\sin\frac{3\pi}{n}\cos 3\left(\pi+\alpha-\frac{\pi}{n}\right)+\cdots\cdots\right\}.$$

By a similar process,

$$e_r=\frac{m}{\pi}\left\{A_1\sin\frac{\pi}{n}\sin\left(\pi+\alpha+\varepsilon-\frac{2\pi}{n}(r-1)-\frac{\pi}{n}\right)\right.$$
$$+\frac{A_3}{3}\sin\frac{3\pi}{n}\sin 3\left(\pi+\alpha-\frac{2\pi}{n}(r-1)-\frac{\pi}{n}\right)+\cdots\cdots\cdots$$
$$\left.+\frac{B_3}{3}\sin\frac{3\pi}{n}\cos 3\left(\pi+\alpha-\frac{2\pi}{n}(r-1)-\frac{\pi}{n}\right)+\cdots\cdots\right\},$$

$$e_0=\frac{m}{2\pi}\int_0^{\pi}\left(A_1\sin(\pi-\varphi+\varepsilon)+A_3\sin 3(\pi-\varphi)+\cdots\cdots\right)d\varphi$$
$$=\frac{m}{\pi}\left(A_1\cos\varepsilon+\frac{A_3}{3}+\frac{A_5}{5}+\cdots\cdots\right).$$

A. *a.* 3. Calculation of necessary constants.

Applying Fourier's series, let

$$\Sigma E=W_0+W_1\sin 2nwt+W_2\sin 2\cdot 2nwt+\cdots\cdots$$
$$+Z_1\cos 2nwt+Z_2\cos 2\cdot 2nwt+\cdots\cdots\cdots$$

Then

$$W_0=\frac{n}{\pi}\left(\sum_1^{\frac{n+1}{2}}r\int_0^{\frac{\pi}{n}}E_{(r)}da-\int_0^{\frac{\pi}{n}}aE_{(1)}da+\int_0^{\frac{\pi}{n}}(a-\tfrac{1}{2})E_{\left(\frac{n+1}{2}\right)}da\right),$$

where $E_{(r)}=E_1\sin\left(\pi+a+\beta-\frac{2\pi}{n}(r-1)-\frac{\pi}{n}\right)$

$$+E_3\sin 3\left(\pi+a-\frac{2\pi}{n}(r-1)-\frac{\pi}{n}\right)+\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$+F_3\cos 3\left(\pi+a-\frac{2\pi}{n}(r-1)-\frac{\pi}{n}\right)+\cdots\cdots$, φ being equal to $\pi+\alpha+\beta$,

$$\sum_1^{\frac{n+1}{2}}r\int_0^{\frac{\pi}{n}}E_{(r)}da=E_1\cos\beta+\frac{E_3}{3}+\frac{E_5}{5}+\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots,$$

the coefficients of F's become zero, and

$$-\int_0^{\frac{\pi}{n}} aE_{(1)}da+\int_0^{\frac{\pi}{n}}(a-\tfrac{1}{2})E_{(\frac{n+1}{2})}da=-E_1\cos\beta+E_1\cos\beta\cdot\frac{n}{\pi}\cdot\sin\frac{\pi}{n}$$

$$+\frac{E_3}{3}\cdot\frac{n}{3\pi}\cdot\sin\frac{3\pi}{n}-\frac{E_3}{3}+\frac{E_5}{5}\frac{n}{5\pi}\sin\frac{5\pi}{n}-\frac{E_5}{5}+\cdots\cdots\cdots\cdots\cdots$$

$$\therefore\quad W_0=\left(\frac{n}{\pi}\right)^2E_1\cos\beta\cdot\sin\frac{\pi}{n}+E_3\left(\frac{n}{3\pi}\right)^2\sin\frac{3\pi}{n}+E_5\left(\frac{n}{5\pi}\right)^2\sin\frac{5\pi}{n}+\cdots\cdots$$

By similar process, let

$$\Sigma e=U_0+U_1\sin 2nwt+U_2\sin 2\cdot 2nwt+\cdots\cdots$$
$$+V_1\cos 2nwt+V_2\cos 2\cdot 2nwt+\cdots\cdots,$$

where

$$U_0=\frac{n}{\pi}\left(\sum_1^{\frac{n+1}{2}}r\int_0^{\frac{\pi}{n}}e_rda-\int_0^{\frac{\pi}{n}}ae_1da+\int_0^{\frac{\pi}{n}}(a-\tfrac{1}{2})e_{\frac{n+1}{2}}da\right).$$

But, $$e_r=\frac{m}{\pi}\left\{A_1\sin\frac{\pi}{n}\sin\left(\pi+a+\varepsilon-\frac{2\pi}{n}(r-1)-\frac{\pi}{n}\right)\right.$$

$$+\frac{A_3}{3}\sin\frac{3\pi}{n}\sin 3\left(\pi+a-\frac{2\pi}{n}(r-1)-\frac{\pi}{n}\right)+\cdots\cdots\cdots$$

$$\left.+\frac{B_2}{3}\sin\frac{3\pi}{n}\cos 3\left(\pi+a-\frac{2\pi}{n}(r-1)-\frac{\pi}{n}\right)+\cdots\cdots\right\},$$

$$\sum_1^{\frac{n+1}{2}}re_r=\frac{m}{\pi}\left(A_1\sin\frac{\pi}{n}\cos\varepsilon+\frac{A_3}{3^2}\cdot\sin\frac{3\pi}{n}+\cdots\cdots\cdots\cdots\cdots\right),$$

the coefficients of B's vanish, and

$$-\int_0^{\frac{\pi}{n}} ae_1da+\int_0^{\frac{\pi}{n}}(a-\tfrac{1}{2})e_{\frac{n+1}{2}}da=\frac{m}{\pi}\left(A_1\frac{n}{\pi}\sin\frac{2\pi}{n}\cos\varepsilon-A_1\sin\frac{\pi}{n}\cos\varepsilon\right.$$

$$\left.+\frac{A_3}{3^2}\frac{n}{3\pi}\sin^2\frac{3\pi}{n}-\frac{A_3}{3^2}\sin\frac{3\pi}{n}+\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\right),$$

$$\therefore\quad U_0=\frac{m}{\pi}\left\{A_1\left(\frac{n}{\pi}\sin\frac{\pi}{n}\right)^2\cos\varepsilon+\frac{A_3}{3}\left(\frac{n}{3\pi}\sin\frac{3\pi}{n}\right)^2+\frac{A_5}{5}\left(\frac{n}{5\pi}\sin\frac{5\pi}{n}\right)^2+\cdots\right\}$$

$$=\frac{m}{\pi}\left(A_1k_1\cos\varepsilon+\frac{A_3}{3}k_3+\frac{A_5}{5}k_5+\cdots\cdots\right),$$

where $$k_r=\left(\frac{n}{r\pi}\sin\frac{r\pi}{n}\right)^2.$$

[illegible] 1. Case of even number of phases.

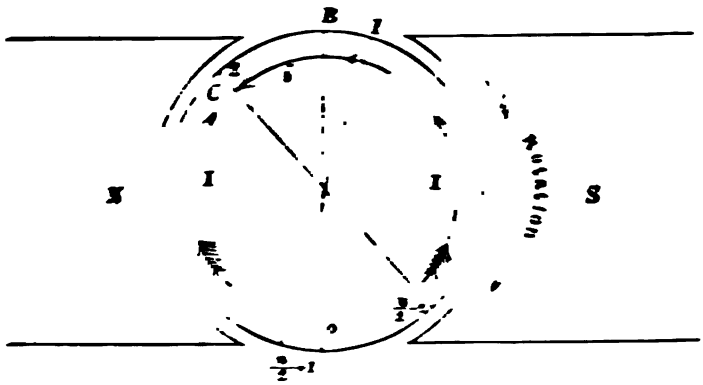


FIG. 5.

Precisely with the same notations, we have for the 1st, 2nd, ... $\frac{n}{2}+1$th phases:

$$L\frac{d}{dt}\{(2a-1)I\}+(2a-1)Ir+L\frac{di_1}{dt}+i_1r+e_1=E_1\sin\varphi+\cdots\cdots,$$

$$-\left(L\frac{dI}{dt}+Ir\right)+L\frac{di_2}{dt}+i_2r+e_2=E_1\sin\left(\varphi-\frac{2\pi}{n}\right)+\cdots\cdots\cdots\cdots\cdots,$$

.....

and $$-L\frac{d}{dt}\{(2a-1)I\}-(2a-1)Ir+L\frac{di_{\frac{n}{2}+1}}{dt}+i_{\frac{n}{2}+1}r+e_{\frac{n}{2}+1}$$

$$=E_1\sin\left(\varphi-\frac{2\pi}{n}\cdot\frac{n}{2}\right)+\cdots\cdots$$

for $0<a<1$.

For external circuit

$$\left(\frac{n}{2}L+2L_e\right)\frac{dI}{dt}+\left(\frac{n}{2}r+2R_e\right)I-\left(L(1-a)\frac{di_1}{dt}+(1-a)i_1r\right.$$

$$\left.+L\frac{di_2}{dt}+i_2r+\cdots\cdots+La\frac{di_{\frac{n}{2}+1}}{dt}+ai_{\frac{n}{2}+1}r\right)=e_0-c,$$

i. e. $$\lambda'\frac{dI}{dt}+\rho'I-\left(L\frac{dI}{dt}+Ir\right)(1-2a)^2+2LkI(1-2a)$$

$$=e_0-c+\Sigma E-\Sigma e,$$

where $$\lambda'=L+2L_e,\qquad \rho'=r+2R_e.$$

Now, as before, putting

$$\lambda_2=\lambda'-\frac{L}{3}, \qquad \rho_2=\rho'-\frac{r}{3}$$

$$\lambda_2\frac{dI}{dt}+I\cdot\rho_2=e_0-c+\Sigma E-\Sigma e \text{.....(VIII).}$$

At $a=1$ the armature has revolved through a space $\frac{2\pi}{n}$ and the condition becomes the same as at the time at which the rotation began, or $a=0$.

Therefore, in this case we must suppose $\Sigma E-\Sigma e$ as periodic functions, with a period n times that of the E. M. F's, or applied voltage.

A. *b.* 2. Calculation of necessary constants.

Applying Fourier's series:

$$\Sigma E=W_0+W_1\sin nwt+W_2\sin 2nwt+\cdots\cdots$$
$$+Z_1\cos nwt+Z_2\cos 2nwt+\cdots\cdots$$

where

$$W_0=\frac{n}{2\pi}\left(\sum_1^{\frac{n}{2}+1} r\int_0^{\frac{2\pi}{n}} E_{(r)}da+\int_0^{\frac{2\pi}{n}}(a-1)E_{\left(\frac{n}{2}+1\right)}da-\int_0^{\frac{2\pi}{n}} aE_{(1)}da\right).$$

But, $$\sum_1^{\frac{n}{2}+1} r\int_0^{\frac{2\pi}{n}} E_{(r)}da=2E_1\cos\beta\cdot\cos\frac{\pi}{n}+2\frac{E_3}{3}\cos\frac{3\pi}{n}+\cdots\cdots,$$

$$-\int_0^{\frac{2\pi}{n}} aE_{(1)}da+\int_0^{\frac{2\pi}{n}}(a-1)E_{\left(\frac{n}{2}+1\right)}da=2E_1\cos\beta\cdot\frac{n}{\pi}\cdot\sin\frac{\pi}{n}$$
$$-2E_1\cos\beta\cdot\cos\frac{\pi}{n}+\frac{2E_3n}{3^2\pi}\cdot\sin\frac{3\pi}{n}-\frac{2E_3}{3}\cdot\cos\frac{3\pi}{n}+\cdots\cdots,$$

and the coefficients of F's vanish.

$$\therefore\quad W_0=E_1\left(\frac{n}{\pi}\right)^2\cos\beta\sin\frac{\pi}{n}+E_3\left(\frac{n}{3\pi}\right)^2\sin\frac{3\pi}{n}+E_5\left(\frac{n}{5\pi}\right)^2\sin\frac{5\pi}{n}+\cdots.$$

Similarly, let

$$\Sigma e=U_0+U_1\sin nwt+U_2\sin 2nwt+\cdots\cdots$$
$$+V_1\cos nwt+V_2\cos 2nwt+\cdots\cdots,$$

then

$$U_0=\frac{m}{\pi}\left\{A_1\left(\frac{n}{\pi}\sin\frac{\pi}{n}\right)^2\cos\varepsilon+\frac{A_3}{3}\cdot\left(\frac{n}{3\pi}\sin\frac{3\pi}{n}\right)^2+\frac{A_5}{5}\left(\frac{n}{5\pi}\sin\frac{5\pi}{n}\right)^2+\cdots\right\}$$
$$=\frac{m}{n}\left(A_1k_1\cos\varepsilon+\frac{A_3}{3}k_3+\cdots\cdots\right).$$

A. *c*. Solution of the equations obtained in the cases *a*, *b*.

From the equations (VII), (VIII), i.e.

$$\text{(VII)}\quad \lambda_1\frac{dI}{dt}+I\rho_1=e_0-c+\Sigma E-\Sigma e$$

$$=e_0-c+W_0-U_0+(W_1-U_1)\sin 2nwt+(W_2-U_2)\sin 4nwt+\cdots\cdots$$
$$+(Z_1-V_1)\cos 2nwt+(Z_2-V_2)\cos 4nwt+\cdots\cdots,$$

$$\text{(VIII)}\quad \lambda_2\frac{dI}{dt}+I\rho_2=e_0-c+\Sigma E-\Sigma e$$

$$=e_0-c+W_0-U_0+(W_1-U_1)\sin nwt+(W_2-U_2)\sin 2nwt+\cdots\cdots$$
$$+(Z_1-V_1)\cos nwt+(Z_2-V_2)\cos 2nwt+\cdots\cdots,$$

we have the following solutions:

From (VII),

$$I=\frac{W_0+e_0-U_0-c}{\rho_1}+\frac{(W_1-U_1)}{\sqrt{\lambda_1\cdot 2nw^2+\rho_1^2}}\sin\left(2nwt-\tan^{-1}\frac{\lambda_1\cdot 2nw}{\rho_1}\right)$$
$$+\frac{(W_2-U_2)}{\sqrt{\lambda_1\cdot 4nw^2+\rho_1^2}}\sin\left(4nwt-\tan^{-1}\frac{\lambda_1\cdot 4nw}{\rho_1}\right)$$
$$+\cdots\cdots+\frac{(Z_1-V_1)}{\sqrt{\lambda_1\cdot 2nw^2+\rho_1^2}}\cos\left(2nwt-\tan^{-1}\frac{\lambda_1\cdot 2nw}{\rho_1}\right)$$
$$+\frac{(Z_2-V_2)}{\sqrt{\lambda_1\cdot 4nw^2+\rho_1^2}}\cos\left(4nwt-\tan^{-1}\frac{\lambda_1\cdot 4nw}{\rho_1}\right)+\cdots\cdots$$

From (VIII),

$$I=\frac{W_0+e_0-U_0-c}{\rho_2}+\frac{(W_1-U_1)}{\sqrt{\lambda_2\cdot nw^2+\rho_2^2}}\sin\left(nwt-\tan^{-1}\frac{\lambda_2\cdot nw}{\rho_2}\right)$$
$$+\frac{(W_2-U_2)}{\sqrt{\lambda_2\cdot 2nw^2+\rho_2^2}}\sin\left(2nwt-\tan^{-1}\frac{\lambda_2\cdot 2nw}{\rho_2}\right)$$
$$+\cdots\cdots+\frac{(Z_1-V_1)}{\sqrt{\lambda_2\cdot nw^2+\rho_2^2}}\cos\left(nwt-\tan^{-1}\frac{\lambda_2\cdot nw}{\rho_2}\right)$$
$$+\frac{(Z_2-V_2)}{\sqrt{\lambda_2\cdot 2nw^2+\rho_2^2}}\cos\left(2nwt-\tan^{-1}\frac{\lambda_2\cdot 2nw}{\rho_2}\right)+\cdots\cdots$$

Therefore, the mean values of the terminal voltages for the two cases are respectively

$$c+\frac{(W_0+e_0-U_0-c)}{\rho_1}\cdot 2R_e \text{ and } c+\frac{(W_0+e_0-U_0-c)}{\rho_2}\cdot 2R_e,$$

i. e.

denoting the mean value of the currents in two cases with I_D, we have

the terminal voltage $= W_0 + e_0 - U_0 - I_D(\rho_1 - 2R_e)$.....for (VII)

$= W_0 + e_0 - U_0 - I_D(\rho_2 - 2R_e)$..... „ (VIII)

$= W_0 + e_0 - U_0 - I_D \cdot \frac{2}{3} r$ for both (VII), VIII).

B. Alternating current side.

B. *d.* Currents in all phases.

Let n=odd, then to find the currents in all phases, we must solve the equations (I), (II) with respect to $i_1, i_2 \cdots\cdots i_n$, i. e.

$$
(\mathrm{I})\begin{cases}
L\dfrac{d\{(2a-1)I\}}{dt} + (2a-1)Ir + L\dfrac{di_1}{dt} + i_1 r + e_1 = E_1 \sin\varphi + \cdots\cdots, \\
-\left(L\dfrac{dI}{dt} + Ir\right) + L\dfrac{di_2}{dt} + i_2 r + e_2 = E_1 \sin\left(\varphi - \dfrac{2\pi}{n}\right) + \cdots\cdots, \\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
\pm\left(L\dfrac{dI}{dt} + Ir\right) + L\dfrac{di_r}{dt} + i_r r + e_r = E_1 \sin\left(\varphi - \dfrac{2\pi}{n}(r-1)\right) + \cdots\cdots, \\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
-\left(L\dfrac{d(2aI)}{dt} + 2aIr\right) + L\dfrac{di_{\frac{n+1}{2}}}{dt} + i_{\frac{n+1}{2}} r + e_{\frac{n+1}{2}} \\
\qquad = E_1 \sin\left(\varphi - \dfrac{2\pi}{n}\,\dfrac{(n-1)}{2}\right) + \cdots\cdots.
\end{cases}
$$

$$
(\mathrm{II})\begin{cases}
L\dfrac{d(2aI)}{dt} + 2aIr + L\dfrac{di_1}{dt} + i_r r + e_1 = E_1 \sin\varphi' + \cdots\cdots, \\
-\left(L\dfrac{dI}{dt} + Ir\right) + L\dfrac{di_2}{dt} + i_2 r + e_2 = E_1 \sin\left(\varphi' - \dfrac{2\pi}{n}\right) + \cdots\cdots, \\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
\pm\left(L\dfrac{dI}{dt} + Ir\right) + L\dfrac{di_r}{dt} + i_r r + e_r = E_1 \sin\left(\varphi' - \dfrac{2\pi}{n}(r-1)\right) + \cdots\cdots, \\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
-\left(L\dfrac{d}{dt}\{(2a-1)I\} + (2a-1)Ir\right) + L\dfrac{di_{\frac{n+1}{2}+1}}{dt} + i_{\frac{n+1}{2}+1} r + e_{\frac{n+1}{2}+1} \\
\qquad = E_1 \sin\left(\varphi' - \dfrac{2\pi}{n}\,\dfrac{(n+1)}{2}\right) + \cdots\cdots,
\end{cases}
$$

so long as $0 < a < \frac{1}{2}$.

When solving these equations, it may easily be seen that i_1, i_2, ...i_n contain the harmonics $\sin 2nwt$, $\cos 2nwt$, $\sin 4nwt$, $\cos 4nwt$, ..., as I contains them. Assuming these harmonics to be small, so that the current in the direct current side is a true direct current I_0, and E's and e's are sinusoidal, we have

$$
\text{(IX)}\begin{cases}
I_0\{(2a-1)r+2Lk\}+L\dfrac{di_1}{dt}+i_1r+e_1=E_1\sin\varphi, \\
-I_0r+L\dfrac{di_2}{dt}+i_2r+e_2=E_1\sin\left(\varphi-\dfrac{2\pi}{n}\right), \\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
\pm I_0r+L\dfrac{di_r}{dt}+i_rr+e_r=E_1\sin\left(\varphi-\dfrac{2\pi}{n}(r-1)\right), \\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
-I_0(2ar+2Lk)+L\dfrac{di_{\frac{n+1}{2}}}{dt}+i_{\frac{n+1}{2}}r+e_{\frac{n+1}{2}}=E_1\sin\left(\varphi-\dfrac{2\pi}{n}\dfrac{(n-1)}{2}\right),
\end{cases}
$$

where e_r has the form $\varepsilon_1\sin\left(\varphi_1-\dfrac{2\pi}{n}(r-1)\right)$, and from (II)

$$
\text{(X)}\begin{cases}
I_0(2ar+2Lk)+L\dfrac{di_1}{dt}+i_1r+e_1=E_1\sin\varphi', \\
-I_0r+L\dfrac{di_2}{dt}+i_2r+e_2=E_1\sin\left(\varphi'-\dfrac{2\pi}{n}\right), \\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
\pm I_0r+L\dfrac{di_r}{dt}+i_rr+e_r=E_1\sin\left(\varphi'-\dfrac{2\pi}{n}(r-1)\right), \\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
-I_0\{(2a-1)r+2Lk\}+L\dfrac{di_{\frac{n+1}{2}+1}}{dt}+i_{\frac{n+1}{2}+1}r+e_{\frac{n+1}{2}+1} \\
\qquad =E_1\sin\left(\varphi'-\dfrac{2\pi}{n}\dfrac{(n+1)}{2}\right),
\end{cases}
$$

where e_r has the form $\varepsilon_1\sin\left(\varphi'_1-\dfrac{2\pi}{n}(r-1)\right)$.

Then solving (IX),

$$
i_1=\frac{E_1\sin\left(\varphi-\tan^{-1}\dfrac{Lw}{r}\right)-\varepsilon_1\sin\left(\varphi_1-\tan^{-1}\dfrac{Lw}{r}\right)}{\sqrt{Lw^2+r^2}}-I_0\cdot(2a-1),
$$

$$i_2=\frac{E_1\sin\left(\varphi-\tan^{-1}\frac{Lw}{r}-\frac{2\pi}{n}\right)-\varepsilon_1\sin\left(\varphi_1-\tan^{-1}\frac{Lw}{r}-\frac{2\pi}{n}\right)}{\sqrt{\overline{Lw}^2+r^2}}+I_0,$$

.....

$$i_{\frac{n+1}{2}}=\frac{E_1\sin\left(\varphi-\tan^{-1}\frac{Lw}{r}-\frac{2\pi}{n}\frac{(n-1)}{2}\right)-\varepsilon_1\sin\left(\varphi_1-\tan^{-1}\frac{Lw}{r}-\frac{2\pi}{n}\frac{(n-1)}{2}\right)}{\sqrt{\overline{Lw}^2+r^2}}$$

$$+I_0\cdot 2a.$$

And solving (X),

$$i_1=\frac{E_1\sin\left(\varphi'-\tan^{-1}\frac{Lw}{r}\right)-\varepsilon_1\sin\left(\varphi'_1-\tan^{-1}\frac{Lw}{r}\right)}{\sqrt{\overline{Lw}^2+r^2}}-I_0\cdot 2a,$$

$$i_2=\frac{E_1\sin\left(\varphi'-\tan^{-1}\frac{Lw}{r}-\frac{2\pi}{n}\right)-\varepsilon_1\sin\left(\varphi'_1-\tan^{-1}\frac{Lw}{r}-\frac{2\pi}{n}\right)}{\sqrt{\overline{Lw}^2+r^2}}+I_0,$$

.....

$$i_{\frac{n+1}{2}+1}=\frac{E_1\sin\left(\varphi'-\tan^{-1}\frac{Lw}{r}-\frac{2\pi}{n}\frac{(n+1)}{2}\right)-\varepsilon_1\sin\left(\varphi'_1-\tan^{-1}\frac{Lw}{r}-\frac{2\pi}{n}\frac{(n+1)}{2}\right)}{\sqrt{\overline{Lw}^2+r^2}}$$

$$+I_0(2a-1),$$

i. e. in simplified forms,

$$\begin{cases} i_1=C_1-I_0(2a-1), \\ i_2=C_2+I_0, \\ \dots\dots\dots\dots \\ i_r=C_r\pm I_0, \\ \dots\dots\dots\dots \\ i_{\frac{n+1}{2}}=C_{\frac{n+1}{2}}+I_0\cdot 2a. \end{cases} \qquad \begin{cases} i_1=C'_1-I_0\cdot 2a, \\ i_2=C'_2+I_0, \\ \dots\dots\dots\dots \\ i_r=C'_r\pm I_0, \\ \dots\dots\dots\dots \\ i_{\frac{n+1}{2}+1}=C'_{\frac{n+1}{2}+1}+I_0(2a-1). \end{cases}$$

B. *e.* Currents in all leads.

In the first lead (Fig. 5) the current is i_1-i_n,
or $C_1-C_n-I_0(2a-2)$, supposing $n>3$,
in the second lead,
$C_2-C_1+I_0\cdot 2a$,
in the rth lead,
C_r-C_{r-1},

in the $\frac{n+1}{2}$th lead,

$$C_{\frac{n+1}{2}} - C_{\frac{n-1}{2}} + I_0(2a-1),$$

in the $\frac{n+1}{2}+1$th lead,

$$C_{\frac{n+1}{2}+1} + C_{\frac{n+1}{2}} - I_0(2a+1),$$

for the equation (IX).

For the equation (X), we have
in the first lead,

$$C'_1 - C'_n + I_0(1-2a),$$

in the second lead,

$$C'_2 - C'_1 + I_0(1+2a),$$

in the rth lead,

$$C'_r - C'_{r-1},$$

in the $\frac{n+1}{2}+1$th lead,

$$C'_{\frac{n+1}{2}+1} - C'_{\frac{n+1}{2}} + I_0(2a-2),$$

in the $\frac{n+1}{2}+2$th lead,

$$C'_{\frac{n+1}{2}+2} - C_{\frac{n+1}{2}+1} - I_0 \cdot 2a.$$

If $n=3$, the current of the first lead is

$$C_1 - C_3 - I_0(2a-2) \quad \text{or} \quad C'_1 - C'_3 - I_0(4a-1)$$

in the second lead,

$$C_2 - C_1 - I_0(4a-1) \quad \text{or} \quad C'_2 - C'_1 + I_0(2a+1)$$

in the third lead,

$$C_3 - C_2 - I_0(2a+1) \quad \text{or} \quad C'_3 - C'_2 + I_0(2a-2).$$

Thus, even though the E. M. F's are all sinusoidal and the machine produces a true direct current, the currents in the leads of the alternating current side are distorted from a sinusoidal form by a varying current.

Now, if the rotary converter be fed with long transmission lines, the solution becomes somewhat different from the above. Let the generator be assumed to have a ring connection, and $n=$odd,

>3, then the whole system, when diagramatically shown, becomes as follows:

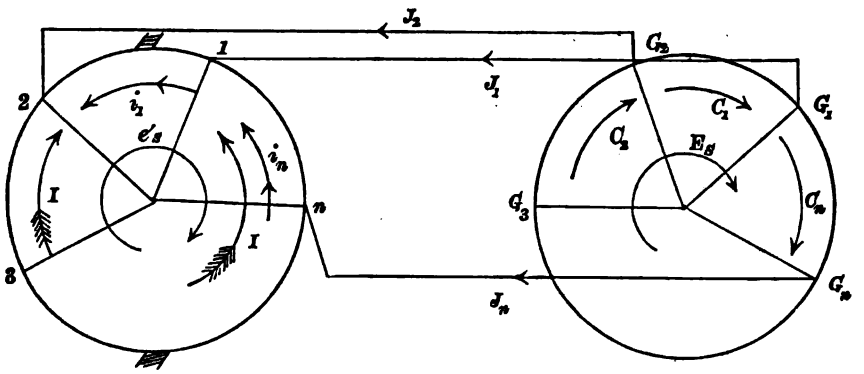


FIG. 6.

Let

the currents in all leads $=J_1, J_2, \cdots\cdots J_n$,

the currents in all phases of generator $=C_1, C_2, \cdots\cdots C_n$,

the direction of these currents being shown by arrows, and the coefficient of self-induction of one lead $=L'_l$,

that of one phase of generator $=L_g$,

the resistance of each lead $=R$,

that of one phase of generator $=r_g$,

E. M. F. induced in the rth phase of generator $=E_r$,

" " " " " " " converter $=e_r$,

the direction of these E. M. F's being represented by the arrows.

Let the coefficient of mutual induction between any two leads $=M$,

then $L'_l - M = L_l$, and $L_l \frac{d}{dt} + R = D_l$; $L \frac{d}{dt} + r = D_r$; $L_g \frac{d}{dt} + r_g = D_g$.

Now, assuming the same coefficient of mutual induction between any two leads, we have, as to the circuit $G_1 - 1 - 2 - G_2$

$$D_l J_1 + D_r i_1 + D_r\{(2a-1)I\} - D_l J_2 + D_g C_1 = E_1 - e_1 \ldots\ldots (1),$$

for $G_2 - 2 - 3 - G_3$

$$D_l J_2 + D_r i_2 - D_r I - D_l J_3 + D_g C_2 = E_2 - e_2 \ldots\ldots\ldots\ldots\ldots\ldots (2).$$

Subtracting (1) from (2), since $i_2-i_1=C_2-C_1=J_2$, we have:

$$-D_lJ_1+2D_lJ_2+D_rJ_2-D_r(2aI)-D_lJ_3+D_gJ_2=(E_2-e_2)-(E_1-e_1),$$

i.e. $-D_lJ_1+(2D_l+D_r+D_g)J_2-D_lJ_3=(E_2-e_2)-(E_1-e_1)+D_r(2aI)$.

Similarly, during the time that the armature revolves through $\frac{\pi}{n}$ from the brush, we have:

$$-D_lJ_2+(2D_l+D_r+D_g)J_3-D_lJ_4=(E_3-e_3)-(E_2-e_2),$$

.....

$$-D_lJ_{\frac{n-1}{2}}+(2D_l+D_r+D_g)J_{\frac{n+1}{2}}-D_lJ_{\frac{n+1}{2}+1}$$
$$=(E_{\frac{n+1}{2}}-e_{\frac{n+1}{2}})-(E_{\frac{n-1}{2}}-e_{\frac{n-1}{2}})+D_r\{(2a-1)I\},$$

$$-D_lJ_{\frac{n+1}{2}}+(2D_l+D_r+D_g)J_{\frac{n+1}{2}+1}-D_lJ_{\frac{n+1}{2}+2}$$
$$=(E_{\frac{n+1}{2}+1}-e_{\frac{n+1}{2}+1})-(E_{\frac{n+1}{2}}-e_{\frac{n+1}{2}})-D_r\{(2a+1)I\},$$

.....

$$-D_lJ_n+(2D_l+D_r+D_g)J_1-D_lJ_2=(E_1-e_1)-(E_n-e_n)-D_r\{(2a-2)I\}.$$

If we put,

$$J_1=j_1+k_1,$$
$$J_2=j_2+k_2,$$
$$\cdots\cdots\cdots\cdots$$
$$J_n=j_n+k_n,$$

and the j's be so chosen that they satisfy

$$(\mathrm{A})\begin{cases} -D_lj_1+(2D_l+D_r+D_g)j_2-D_lj_3=(E_2-e_2)-(E_1-e_1), \\ -D_lj_2+(2D_l+D_r+D_g)j_3-D_lj_4=(E_3-e_3)-(E_2-e_2), \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ -D_lj_{\frac{n-1}{2}}+(2D_l+D_r+D_g)j_{\frac{n+1}{2}}-D_lj_{\frac{n+1}{2}+1} \\ \qquad\qquad =(E_{\frac{n+1}{2}}-e_{\frac{n+1}{2}})-(E_{\frac{n-1}{2}}-e_{\frac{n-1}{2}}), \\ -D_lj_{\frac{n+1}{2}}+(2D_l+D_r+D_g)j_{\frac{n+1}{2}+1}-D_lj_{\frac{n+1}{2}+2} \\ \qquad\qquad =(E_{\frac{n+1}{2}+1}-e_{\frac{n+1}{2}+1})-(E_{\frac{n+1}{2}}-e_{\frac{n+1}{2}}), \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ -D_lj_n+(2D_l+D_r+D_g)j_1-D_lj_2=(E_1-e_1)-(E_n-e_n), \end{cases}$$

then k's must satisfy

$$
(\mathrm{B})\begin{cases}
-D_l k_1+(2D_l+D_r+D_g)k_2-D_l k_3=D_r(2aI),\\
-D_l k_2+(2D_l+D_r+D_g)k_3-D_l k_4=0,\\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\
-D_l k_{\frac{n-1}{2}}+(2D_l+D_r+D_g)k_{\frac{n+1}{2}}-D_l k_{\frac{n+1}{2}+1}=D_r\{(2a-1)I\},\\
-D_l k_{\frac{n+1}{2}}+(2D_l+D_r+D_g)k_{\frac{n+1}{2}+1}-D_l k_{\frac{n+1}{2}+2}=-D_r\{(2a+1)\},\\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\
-D_l k_n+(2D_l+D_r+D_g)k_1-D_l k_2=-D_r\{(2a-2)I\}.
\end{cases}
$$

During the time that the armature rotates from $\frac{\pi}{n}$ to $\frac{2\pi}{n}$, we have by similar process:

$$
(\mathrm{C})\begin{cases}
-D_l j_1+(2D_l+D_r+D_g)j_2-D_l j_3=(E_2-e_2)-(E_1-e_1),\\
-D_l j_2+(2D_l+D_r+D_g)j_3-D_l j_4=(E_3-e_3)-(E_2-e_2),\\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\
-D_l j_{\frac{n+1}{2}}+(2D_l+D_r+D_g)j_{\frac{n+1}{2}}-D_l j_{\frac{n+1}{2}+1}\\
\qquad\qquad =(E_{\frac{n+1}{2}}-e_{\frac{n+1}{2}})-(E_{\frac{n-1}{2}}-e_{\frac{n-1}{2}}),\\
-D_l j_{\frac{n+1}{2}}+(2D_l+D_r+D_g)j_{\frac{n+1}{2}+1}-D_l j_{\frac{n+1}{2}+2}\\
\qquad\qquad =(E_{\frac{n+1}{2}+1}-e_{\frac{n+1}{2}+1})-(E_{\frac{n+1}{2}}-e_{\frac{n+1}{2}}),\\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\
-D_l j_n+(2D_l+D_r+D_g)j_1-D_l j_2=(E_1-e_1)-(E_n-e_n),
\end{cases}
$$

and

$$
(\mathrm{D})\begin{cases}
-D_l k_1+(2D_l+D_r+D_g)k_2-D_l k_3=D_r\{(1+2a)I\},\\
-D_l k_2+(2D_l+D_r+D_g)k_3-D_l k_4=0,\\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\
-D_l k_{\frac{n+1}{2}}+(2D_l+D_r+D_g)k_{\frac{n+1}{2}+1}-D_l k_{\frac{n+1}{2}+2}=D_r\{(2a-2)I\},\\
-D_l k_{\frac{n+1}{2}+1}+(2D_l+D_r+D_g)k_{\frac{n+1}{2}+2}-D_l k_{\frac{n+1}{2}+3}=-D_r(2aI),\\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\
-D_l k_n+(2D_l+D_r+D_g)k_1-D_l k_2=-D_r\{(2a-1)I\}.
\end{cases}
$$

Thus, it may be seen from the equations (B) and (D) that the E. M. F. applied in the circuit $G_1-1-3-G_3$, for causing the currents k_1, k_2, k_3 in the circuit, varies as the following scheme:

Angle of rotation of armature from the brush.	0	$\frac{\pi}{n}$	$\frac{2\pi}{n}$
E. M. F. applied in the circuit $G_1-1-3-G_3$.	$D_r(2aI)$ $=I_0(2ar+2Lk)$,	$D_r\{(2a+1)I\}$ $=I_0\{(2a+1)r+2Lk\}$,	

$\frac{2\pi}{n}$	$\frac{3\pi}{n}$	$\frac{4\pi}{n}$	$\frac{5\pi}{n}$
$-D_r\{(2a-2)I\}$ $=-I_0\{(2a-2)+2Lk\}$,	$-D_r\{2a-1)I\}$ $=-I_0\{(2a-1)+2Lk\}$,	0	

$\frac{5\pi}{n}$	$\frac{6\pi}{n}$ ..... $\frac{2\pi}{n}\left(\frac{n-1}{2}\right)$	π
0	0	0

π	$\frac{2\pi}{n}\left(\frac{n+1}{2}\right)$	$\frac{\pi}{n}(n+2)$	$\frac{\pi}{n}(n+3)$
$-D_r(2aI)$ $=-I_0(2ar+2Lk)$,	$-D_r\{(2a+1)I\}$ $=-I_0\{(2a+1)r+2Lk\}$,	$D_r\{(2a-2)I\}$ $=I_0\{(2a-2)r+2Lk\}$,	

$\frac{\pi}{n}(n+3)$	$\frac{\pi}{n}(n+4)$ ..... $\frac{2\pi}{n}(2n-1)$	2π
$D_r\{(2a-1)I\}$ $=I_0\{(2a-1)r+2Lk\}$,	0	0

Thus the applied E. M. F. for causing the k's to flow, is a complex alternating one, with a period equal to one revolution of the armature, and will be obtained from the equations (B) and (D), but their expressions, as is easily seen, are very complicated.

The equations (A) and (B) can be obtained when the converter is working as a pure synchronous motor, with the same generator E. M. F., E's, and the counter E. M. F., e's. Therefore, the currents j's are those taken by the converter when it is considered as a pure synchronous motor.

Hence, we see, as regards the currents in the leads, that, unless $D_r(2aI)$, etc., are negligible, the converter cannot be taken as the same as the synchronous motor.

In the case $n=3$, the equations for k's become:

$$(\mathrm{E})\begin{cases}-D_l k_1+(2D_l+D_r+D_g)k_2-D_l k_3=D_r\{(4a-1)I\},\\ -D_l k_2+(2D_l+D_r+D_g)k_3-D_l k_1-D_l k_1=-D_r\{(2a+1)I\},\\ -D_l k_3+(2D_l+D_r+D_g)k_1-D_l k_2=-D_r\{(2a-2)I\},\end{cases}$$

and

$$(\mathrm{F})\begin{cases}-D_l k_1+(2D_l+D_r+D_g)k_1-D_l k_3=D_r\{(2a+1)I\},\\ -D_l k_2+(2D_l+D_r+D_g)k_3-D_l k_1=D_r\{(2a-2)I\},\\ -D_l k_3+(2D_l+D_r+D_g)k_1-D_l k_2=-D_r\{(4a-1)I\}.\end{cases}$$

From (E):

$$\begin{vmatrix}-D_l, & 2D_l+D_r+D_g, & -D_l\\ -D_l, & -D_l & 2D_l+D_r+D_g\\ +(2D_l+D_r+D_g), & -D_l & -D_l\end{vmatrix} k_1$$

$$=\begin{vmatrix}D_r\{(4a-1)I\}, & 2D_l+D_r+D_g, & -D_l\\ -D_r\{(2a+1)I\}, & -D_l, & 2D_l+D_r+D_g\\ -D_r\{(2a-2)I\}, & -D_l, & -D_l\end{vmatrix},$$

$$\therefore\quad k_1=\frac{-D_r\{(2a-1)I)}{3D_l+D_r+D_g}$$

$$=\frac{-I_0\{(2a-2)r+2Lk)}{3R+r+r_g}=\frac{I_0.2kr(3L_l+L_g+L)}{(3R+r+r_g)^2}.$$

Similarly, $k_2=\dfrac{D_r\{(4a-1)I)}{3D_l+D_r+D_g}$

$$=\frac{I_0(4a-1)r+4Lk)}{3K+r+r_g}-\frac{I_0(4kr(3L_l+L_g+L)}{(3R+r+r_g)^2};$$

$$k_3=\frac{D_r\{(2a+1)I\}}{3D_l+D_r+D_g}$$

$$=\frac{-I_0\{(2a+1)r+2Lk\}}{3R+r+r_g}+\frac{I_0 2kr(3L_l+L_g+L)}{(3R+r+r_g)^2}.$$

Similarly from (F):

$$k_1=\frac{-D_r\{(4a-1)I\}}{3D_l+D_r+D_g}=\frac{-I_0\{(4a-1)\}}{3R+r+r_g}+\frac{I_0\cdot 4kr(3L_l+L_g+L)}{(3R+r+r_g)^2};$$

$$k_2=\frac{D_r\{(2a+1)I\}}{3D_l+D_r+D_g}=\frac{I_0\cdot\{(2a+1)r+2Lk)}{3R+r+r_g}-\frac{I_0\cdot 2kr(3L_l+L_g+L)}{(3R+r+r_g)^2};$$

$$k_3=\frac{D_r\{(2a-2)I\}}{3D_l+D_r+D_g}=\frac{I_0\{(2a-2)r+2Lk\}}{3R+r+r_g}-\frac{I_0\cdot 2kr(3L_l+L_g+L)}{(3R+r+r_g)^2}.$$

Thus, the current in the first phase varies, during one rotation of the armature, according to the following scheme:

(a)	Angle of rotation of armature from the brush.	0	$\frac{2\pi}{6}$	$\frac{2\pi}{6}\cdot 2$	$\frac{2\pi}{6}\cdot 3$	$\frac{2\pi}{6}\cdot 3$	$\frac{2\pi}{6}\cdot 4$	$\frac{2\pi}{6}\cdot 5$	$\frac{2\pi}{6}\cdot 6$
(b)	Current in the first phase (except the value at $\frac{2\pi}{6}\cdot r$, where $r=1, 2 \ldots 6$).	k_1 of (E),	k_1 of (F),	k_3 of (E),	k_3 of (F),	k_2 of (E),	k_2 of (F).		

Thus far, we have considered the case n=odd, but similar relations exist in the case of n=even.

As they are not of very much importance, the deductions for them will be omitted.

C. Inferences from the results.

From the above results, we see that:

1. The current in the direct current side is not a true direct current, but a pulsating one in general, though the effect of the asymmetry of the magnetic disposition, the fluctuation of the angular velocity, and the limited number of the commutater segments, etc., are absent.

2. The period of pulsation is 2n times or n times that of the applied voltage, according as the number of phases is odd or even, n denoting the number of phases.

3. In the term $U_0 - e_0$ or $\frac{m}{\pi}A_1 \cos \varepsilon(1-k_1) + \frac{m}{\pi}\frac{A_3}{3}(1-k_3) + \cdots\cdots\cdots$, contained in the expression of the terminal voltage, $1-k_1$, $1-k_3, \cdots\cdots\cdots$are not large quantities; moreover, the effect of the armature reaction is always to oppose the change of the excitation as in the synchronous motor, and, therefore, the change of the excitation cannot be effective for the change of the mean value of the direct current side voltage.

4. When feeding a circuit of comparatively low resistance,

such as the case of battery charging, since the expressions of the fluctuating part do not contain the counter E. M. F. (supposed constant), but the resistance and self-induction only, the fluctuation must be larger than that in the case of feeding a circuit with high resistance and self-induction, though the mean values of the current in the two cases are the same.

5. The currents in the leads of the alternating current side are different from those in the case of the synchronous motor working under the same conditions, the former being the sum of the latter and a pulsating current which has a period equal to one revolution of the armature, and will become negligible when LI_0, rI_0 are negligibly small.

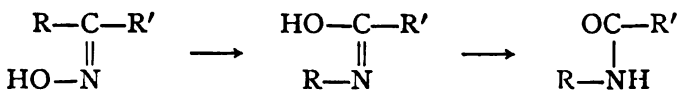
6. Thus, the rotary converter may be looked upon as a combination of a synchronous motor and a direct current generator only when $L\frac{di_r}{dt}+i_r r+\left(L\frac{dI}{dt}+Ir\right)$, $L\frac{d\{(2a-1)I\}}{dt}+I\cdot(2a-1)r$ $+L\frac{di_1}{dt}+i_1 r$ etc. are very small, for in this case $E\cong e$, and, therefore, the machine gives out a true direct current, and the currents in the leads of the alternating current side are the same as in the case of the synchronous motor, as has been stated in (5).

On Beckmann's Rearrangement.

By

Mitsuru Kuhara and **Tadaka Kainoshô.**

A well-known intermolecular reaction, so-called Beckmann's rearrangement which especially occurs in the molecules of oximido compounds, is due to the apparent interchange of position between one of two radicals, linked to carbon, and a hydroxyl group, united to nitrogen, under the action of acetic acid, its anhydride or chloride, as well as through the action of phosphorus pentachloride and water, etc.; resulting in the formation of the substituted acid amides as final products, as is seen in the following scheme:



The investigation of the cause and mechanism of such rearrangement, has always been one of the problems for chemists; but it has not yet been satisfactorily solved.

As a matter of fact; it has already been shown by Beckmann himself and other chemists[1] that the presence of hydrochloric acid greatly facilitates the rearrangement. It may probably act partly as a catalytic agent. For instance: in the case where acetyl chloride is used as a rearranging agent, a small quantity of it is sufficient to convert a large quantity of an oxime into a substituted acid amide; such rearrangement, as the authors assume, may be due in part to the catalytic action of hydrochloric acid, actually generated from acetyl chloride by reacting with the oxime.[2]

[1] Ber. d. chem. Gesell., **20**, 2581; **22**, 433; **27**, 300; Amer. Chem. Journ., **18**, 754.
[2] Compare with Ber. d. chem. Gesell., **26**, 2272; **27**, 300.

In order to see if there may exist some relation between the amount of an oxime and that of acetyl chloride for the intermolecular rearrangement of the former, the authors conducted certain experiments by working with a constant quantity of acetyl chloride upon various quantities of diphenyl ketoxime. Thus, 2, 4, and 8 equivalents of diphenyl ketoxime in chloroform solutions were heated with 1 equivalent of acetyl chloride respectively, for ten hours at a temperature of 100°–110°, and it was found in each experiment that the most part of the oxime actually taken, had been transformed into benzanilide. Hence, we have to confess that the amount of the oxime to be rearranged is not dependent upon the amount of acetyl chloride, or it is better to say, that of hydrochloric acid formed in the reaction since it acts as a catalytic agent.

The authors have, now, to put forward an explanation based upon the assumption that the rearrangement of an oxime by acetyl chloride is due to the mutual exchange of the positions between a positive hydrocarbon radical linked to carbon and a negative radical united to nitrogen, in the acetyl oxime produced, arising from the change of the relative affinities analogous to diphenyl ketoximido chloride,[1] facilitated by the catalytic action of hydrochloric acid generated in the reaction, immediately followed by the formation of a substituted acid amide by the further action of hydrochloric acid which may actually take a part of the reaction, as is seen in the following representations:

(I)

1) $$\begin{array}{c} R-C-R' \\ \| \\ HO-N \end{array} + CH_3COCl = \begin{array}{c} R-C-R' \\ \| \\ CH_3COON \end{array} + HCl$$

2) $$\begin{array}{c} R-C-R' \\ \| \\ CH_3COON \end{array} \xrightarrow[\text{by the catalytic action of HCl}]{} \begin{array}{c} CH_3COO-C-R' \\ \| \\ R-N \end{array}$$

[1] Ber. d. chem. Gesell., **19**, 988; **27**, 301.

$$3)\quad \begin{array}{c} CH_3COO-C-R' \\ \| \\ R-N \end{array} + \begin{array}{c} Cl \\ | \\ H \end{array} = CH_3COCl + \begin{array}{c} OC-R' \\ | \\ R-NH \end{array}$$

The acetyl chloride thus formed in the last stage of the reaction may act upon the fresh part of the oxime forming its ester, as before, with the liberation of hydrochloric acid which again may cause the interchange of the positions of two radicals and in turn bring about the decomposition of an intermediate product to a substituted acid amide, so the same process progressing further until the oxime is exhausted. A trifling amount of acetyl chloride, therefore, must be theoretically possible to convert an infinite quantity of the oxime into a substituted acid amide, apparently acetyl chloride remaining unchanged.

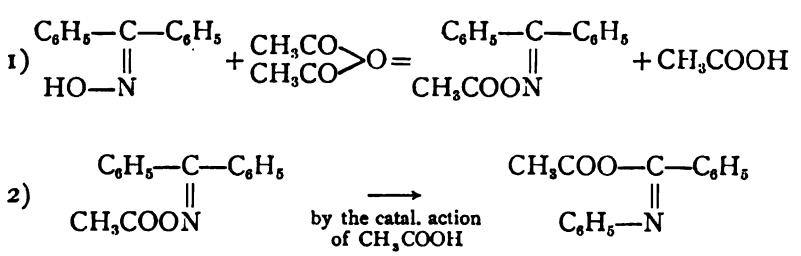
Admitting that hydrochloric acid may actually take a part of the reaction in such a way as already stated, it is to be presumed that when various quantities of hydrochloric acid is allowed to act upon the same definite quantity of a pure oxime ester, the quantities of a rearrangement product or substituted acid amide produced, should be proportional to those of the hydrochloric acid taken, if its quantities be smaller than enough to be equivalent to those of the oxime ester used, as the formation of new hydrochloric acid will not be effected in the case of the ester, the acetyl chloride formed remaining by itself unchanged, but to the quantities of oxime ester, if hydrochloric acid be present more than enough to be equivalent to those of the oxime ester. For the experiments, the authors studied the action of various molecular proportions of hydrochloric acid in its saturated chloroform solution upon a constant molecular quantity of acetyl diphenyl ketoxime, $(C_6H_5)_2C:NO{\cdot}COCH_3$, by heating each mixture in a sealed tube at a definite temperature for the same period of time, and found in fact the production of benzanilide to be approximately proportional to the actually reacting quantities of hydrochloric acid used, as is seen in the following table:

$(C_6H_5)_2C{:}NO{\cdot}COCH_3$ (used).	HCl (used).	$C_6H_5{\cdot}CONH{\cdot}C_6H_5$ (produced).	$C_6H_5{\cdot}CONH{\cdot}C_6H_5$ (to be produced theoretically).
1 mol.	2 mols.	1 mol. approximately.	1 mol.
1 ,,	1 mol.	1 ,, ,,	1 ,,
1 ,,	0·5 ,,	0·5 ,, ,,	0·5 ,,
1 ,,	0·25 ,,	0·25 ,, ,,	0·25 ,,
1 ,,	0·20 ,,	0·20 ,, ,,	0·20 ,,

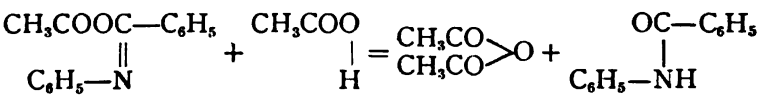
Details will be referred to in the Experimental Part.

With regard to the rearrangement of the oxime by acetic anhydride and by glacial acetic acid, we find in Beckmann's experiments[1] that diphenyl ketoxime undergoes the rearrangement by the large excess of either of those two agents at 180° with the production of a small quantity of benzanilide, the decomposition of a greater part of the oxime taking place. In this case, acetyl diphenyl ketoxime, which ought to be formed from diphenyl ketoxime by interacting with either of these two agents, may actually undergo the rearrangement either by the catalytic action of acetic acid produced in the reaction or by one being used in excess, but slowness of the rearrangement may be attributed to the feeble catalytic action of acetic acid, due to the weakness of its acidity; nevertheless the mechanism may be analogous to that with acetyl chloride, thus:

(II)

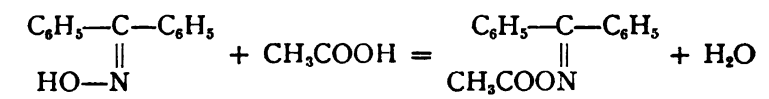


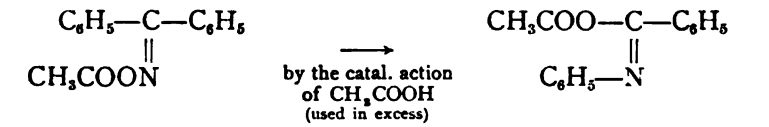
[1] Ber. d. chem. Gesell., **20**, 2580.

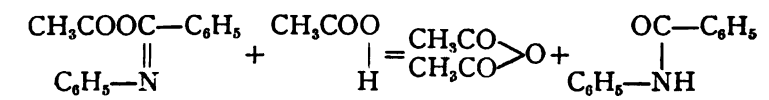


Acetic anhydride formed in the last stage may successively act upon a fresh part of the oxime, it being possible for the reaction to progress further.

(III)







According to Beckmann's experiments,[1] a mixture of glacial acetic acid and acetic anhydride saturated with hydrochloric acid, was found to cause the molecular rearrangement of diphenyl ketoxime and of methyl phenyl ketoxime more readily at much lower temperature, say 100°, than that at which acetic acid or acetic anhydride alone exerts its respective action as stated just above. Now, the authors maintain that hydrochloric acid, which is much stronger in its acidity than acetic acid, will act as a catalytic agent upon the acetyl esters of the oximes, so that the interchange of the positions of the phenyl and the acetic acid radicals may take place readily, and, therefore, the reaction is very likely to follow the mechanism I. already given.

The rearrangement of the oxime by sulphuric acid seems to

[1] Loc. cit.

take place more readily than by acetic acid itself. According to Beckmann[1] methyl phenyl ketoxime (also diphenyl ketoxime) undergoes the rearrangement, at 100°, with five times its weight of conc. sulphuric acid, the final stage of which is stated to be dependent upon the decomposition of an intermediate product by water used, as is seen:

$$\begin{matrix} CH_3 \\ HSO_4 \end{matrix}\!\!>C=NC_6H_5 + H_2O = CH_3CONHC_6H_5 + H_2SO_4$$

It is, however, very probable that, by applying the analogy to this case, the decomposition of an intermediate product may be caused by sulphuric acid itself, just as in the case of other acids previously described, already resulting in the formation of benzanilide before the use of water, as is seen:

$$\begin{matrix} HSO_4-C-CH_3 \\ \| \\ C_6H_5-N \end{matrix} + \begin{matrix} SO_3OH \\ | \\ H \end{matrix} = H_2SO_4 + SO_3 + \begin{matrix} OC-CH_3 \\ | \\ C_6H_5-NH \end{matrix}$$

With regard to the decomposition of an intermediate product by acid, the authors carried out an experiment with benzanilimido chloride, formed from diphenyl ketoxime by phosphorus pentachloride. When the chloride, prepared by the method stated by Beckmann,[2] was allowed to interact with glacial acetic acid mixed with some acetic anhydride, the formation of acetyl chloride and benzanilide immediately took place; hence the reaction may be:

$$\begin{matrix} Cl-C-C_6H_5 \\ \| \\ C_6H_5-N \end{matrix} + \begin{matrix} CH_3COO \\ | \\ H \end{matrix} = CH_3COCl + \begin{matrix} CO-C_6H_5 \\ | \\ C_6H_5NH \end{matrix}$$

Now, the authors, in conclusion, venture to express the opinion that, after all, it is possible the rearrangement of the oxime by acetyl chloride, acetic acid, acetic anhydride, and sulphuric acid,

Ber. d. chem. Gesell., **20**, 1507.
Ibid, **19**, 988.

may all be founded upon analogous mechanism, (though Beckmann doubts the formation of analogous intermediate products in all cases),[1] but its rate may depend upon the degree of acidity of the hydrochloric, sulphuric, or acetic acid, which plays a part in the rearrangement process, just as the commonly accepted view of the catalytic action of acids shows. The relative strength[2] of these three acids as is shown in the following table, by arranging them in the order of their electric conductivity in their equivalent solutions, and of the mean value of the velocity constant of sugar invertion and catalysis of methyl acetate:

	Velocity constant.	Electric conductivity.
Hydrochloric acid	100	100
Sulphuric acid	54	65·1
Acetic acid	0·4	0·4

seems to be concordant with the relative readiness of the rearrangement of the oximes by those acids.

EXPERIMENTAL PART.

I. ACTION OF ACETYL CHLORIDE UPON DIPHENYL KETOXIME.

Different quantities of diphenyl ketoxime were allowed to interact with a smaller, definite quantity of acetyl chloride, and it was observed as a fact that the action of acetyl chloride, so as to cause the rearrangement of the oxime, is independent of the amount of the latter present. In the experiments, 1·39, 2·78, and 5.55 grams of diphenyl ketoxime, or its 2, 4, and 8 equivalents respectively, were mixed with 0·276 gram of acetyl chloride, or its 1 equivalent, dissolved in 5 c. c. of anhydrous chloroform, and heated in a sealed tube at 100°–110° for ten hours. The

[1] Ber. d. chem. Gesell., **27**, 301.

[2] Walker's Phys. Chem., (ed. 1901), p. 279.

content of the tube was evaporated to dryness, when acetyl chloride was noticed by its characteristic odor as being still present; and the residue was treated with hot alcohol. On evaporating the alcoholic solution, the impure benzanilide was left as a residue, which was crystalized from hot benzene and then washed twice with petroleum ether. The benzanilide so obtained was dried and weighed; it may show approximately the whole amount of the rearrangemeat product, the results being represented in the following table:

Number of experiment.	Diphenyl ketoxime		Acetyl chloride		Benzanilide formed	
	taken in gram.	in terms of equivalent.	taken in gram.	in terms of equivalent.	in gram.	per cent.
I.	1·39	2·	0·276	1·	1·09	78·4
II.	2·78	4·	0·276	1·	2·19	78·8
III.	5·55	8·	0·276	1·	4·13	74·4

By inference from the above data, the action of acetyl chloride, or possibly of hydrochloric acid generated, should be merely catalytic, as comparatively a small quantity of acetyl chloride is able to effect the rearrangement of the most part of the oxime present, no matter how large the quantity of the latter may be.

2. ACTION OF HYDROCHLORIC ACID UPON ACETYL DIPHENYL KETOXIME.

2·5 grams of acetyl diphenyl ketoxime[1] dissolved in some chloroform saturated with dry hydrochloric acid, was heated in a sealed tube at 130° for fifteen hours. The content of the tube, when

[1] The authors found it more advantageous to use acetic anhydride for the acetylation of diphenyl ketoxime, while Spiegler recommends the use of acetyl chloride (Monatsh. f. Chem., 5, 205) by which process a greater part of the oxime undergoes rearrangement, as the authors observed. The acetyl diphenyl ketoxime prepared by this method was analysed and its melting point found to be 71°, while Spiegler states it to be 55°.

cooled, was found to assume a slightly brown colour, with some white, scaly crystals suspended on the surface of the liquid. The whole content was subjected to distillation over a water bath, and in the distillate was observed the presence of acetyl chloride, confirmed by its odor as well as by converting it into acetyl-o-toluide. The residue was treated with alcohol, in which it dissolved almost completely, and the solid left behind on evaporating the alcoholic solution (during which process the characteristic odor of acetic and benzoic esters was noticed) was washed with water and then boiled with a 20% solution of caustic potash to remove the oxime and benzoic acid present, and finally dissolved in chloroform, from which solution the white, scaly crystals separated out. The crystals melted at 159° and had all the properties of benzanilide. The aqueous washing, acidified with hydrochloric acid, was found to contain a minute quantity of ammonium chloride and hydroxylamine hydrochloride, and a trace of aniline hydrochloride recognizable by Runge's reaction. From this experiment, it is obvious that, in the rearrangement of the oxime, the formation of its ester and the action of hydrochloric acid are the most necessary conditions.

Next, in order to confirm the opinion that hydrochloric acid must actually take part in the reaction for the decomposition of an intermediate product, the authors conducted experiments in the way described below: Different molecular quantities of hydrochloric acid in chloroform solution were allowed to act upon a certain definite molecular quantity of acetyl diphenyl ketoxime, that is, 2, 1, $\frac{1}{2}$, $\frac{1}{4}$, etc. of the former in terms of mol. to 1 of the latter, in sealed tubes at 120°–150° for fifteen hours. The content of each tube was subjected to distillation, and the distillate was found to contain some acetyl and benzoyl chlorides as in the previous experiment, the presence of the latter being due, perhaps, to the secondary reaction. The residue was treated with hot alcohol, and, on distilling the alcoholic solution so obtained over a water bath, some acetic and benzoic esters were observed to pass over. The residual substance was washed with hot water

three times, and the washing, which had been acidified with hydrochloric acid, contained a minute quantity of ammonium chloride, hydroxylamine hydrochloride, and a trace of aniline hydrochloride, as in the above experiments. The solid left after washing with hot water, consisting of benzanilide and some diphenyl ketoxime, was washed several times with a hot 20% solution of caustic potash, and then repeatedly with water until the alkaline reaction disappeared in the washing. It was, now, perfectly dried and again washed with petroleum ether, and then weighed as the approximate amount of the rearrangement product or benzanilide after drying, as it is difficult to effect the rearrangement of the whole oxime ester and to get the product in pure state. The results of the experiments are given below:

The first series of experiments: heated for 15 hours at 150°.

Number of experiment.	Acetyl diphenyl ketoxime taken in gram.	Hydrochloric acid taken in gram.	Acetyl diphenyl ketoxime in terms of mol.	Hydrochloric acid in terms of mol.	Benzanilide found in gram.	Benzanilide found in terms of mol.
I.	0·720	0·210	1·	2	0·407	0·716
II.	1·440	0·210	1·	1·	1·034	0·935
III.	1·440	0·105	1·	0·5	0·605	0·533
IV.	2·880	0·105	1·	0·25	0·733	0·323

The second series of experiments: heated for 15 hours at 130°.

V.	0·864	0·063	1·	0·5	0·371	0·544
VI.	1·728	0·063	1·	0·25	0·359	0·263
VII.	1·440	0·042	1·	0·20	0·249	0·219

The third series of experiments: heated for 15 hours at 120°.

VIII.	1·445	0·320	1·	1·518	0·930	0·816
IX.	2·890	0·320	1·	0·759	1·703	0·747
X.	1·445	0·080	1·	0·380	0·475	0·418
XI.	2·320	0·128	1·	0·367	0·690	0·379

As is seen in the tables, in each experiment, except I and VIII, approximately as many mol, of benzanilide as of hydrochloric acid used, has been produced as the rearrangement product; but in experiments I and VIII the quantity of hydrochloric acid having been present in excess, that is more mol. than correspond to that of acetyl diphenyl ketoxime, the yield of benzanilide in each exhibits the approximation toward the mol. of acetyl diphenyl ketoxime taken. In the latter case, however, the yield of benzanilide, which ought to be 1 mol. theoretically in each experiment, corresponding to 1 mol. of acetyl diphenyl ketoxime, is little too low; such deviation, the authors think, may be attributed to the secondary decomposition of the oxime ester owing to the presence of hydrochloric acid in excess.

3. ACTION OF ACETIC ACID UPON BENZANILIDIMIDO CHLORIDE.

To a petroleum ether solution of benzanilidimido chloride, prepared according to Beckmann's statement,[1] some glacial acetic acid mixed with $\frac{1}{8}$ its volume of acetic anhydride was added and the mixture vigorously shaken. Petroleum ether was then quickly expelled by warming with hot water, leaving behind the hot acetic acid solution which, on cooling, separated scaly crystals. The crystals melted at 160° and had all the properties of benzanilide. Hence it is evident that an intermediate product in the rearrangement of the oxime ester is decomposed by acetic acid and, perhaps, by other acids into substituted acid amide, but not by hydrochloric acid in this case because the intermediate product contains no oxygynated negative radical.

Further experiments are being carried on with some other oximes; and the authors expect to communicate the results before long.

March, 1907.

[1] Ber. d. chem. Gesell., **19**, 988.

Determination of the Solubility of a Given Substance by Means of Pulfrich's Refractometer.

(PRELIMINARY COMMUNICATION.)

By

Yukichi Osaka.

In the course of a certain experiment, the author had a necessity to be acquainted with the solubility of benzophenone in alcohol. Owing to its volatility, it is not possible to determine its solubility in alcohol by evaporating the solvent; and moreover, so far as we know, there is no simple chemical method for its determination. Thus, some physical method, such as specific gravity determination,[1] must be followed. It has occurred to the author, however, that Pulfrich's refractometer might well be applied to this determination; with less experimental trouble, indeed, than any other physical method. Upon examination, this method proved itself to be as convenient as was expected, and its results are reliable, as will be shown in the following communication.

There is a well-known formula for the relation between the indices of refraction of a mixture and its components; namely:

$$100\frac{n-1}{d}=p_1\frac{n_1-1}{d_1}+p_2\frac{n_2-1}{d_2}+\cdots\cdots,$$

where n and d denote respectively the index of refraction and the density of a mixture and n_1, n_2,····· and d_1, d_2,····· the indices of refraction and the densities of the components whose percentage amounts are p_1, p_2,····· respectively. This formula

[1] *Cf.* Ostwald-Luther, Physiko-chem. Messungen, 284 (1904).

is, however, too complex for the present purpose, at least from the practical standpoint, and moreover not always riliable, so that an empirical formula of simpler form was sought for, and by trial the following was found well-suited for the purpose:

$$ax+bx^2=\delta-\delta'=\Delta$$

where δ represents the angle directly observed on the divided circle in the refractometer when a solvent was examined, δ' that when a solution was examined, Δ the difference between those angles, x the quantity of a solute in grams in 100 c. c. or 100 grams of its solution, and a and b the constants naturally different in each case when x has different meanings.

To find the constants a and b, two different solutions of known compositions are to be prepared, and the pure solvent and the solutions are to be examined in the refractometer. Let Δ_1 and Δ_2 be the values of Δ corresponding to two given values x_1 and x_2 of x, then we have:

$$a=\frac{\Delta_1 x_2^2-\Delta_2 x_1^2}{x_1 x_2^2-x_2 x_1^2}$$

and

$$b=\frac{\Delta_2 x_1-\Delta_1 x_2}{x_1 x_2^2-x_2 x_1^2}.$$

Now, of a given pair of a solute and solvent, the amount of the solute x in a given solution may be calculated from the difference of the observed angles Δ by the following formula:

$$x=-\frac{a}{2b}\pm\sqrt{\frac{\frac{a^2}{4b}-\Delta}{b}},$$

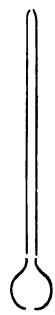
where the lower sign is to be taken when a and b have different signs.

I. BENZOPHENONE IN ALCOHOL.

A given quantity of benzophenone having been put into a weighed measuring flask of 10 c.c. capacity, commercial absolute alcohol was added nearly to the mark, when the solute was

completely dissolved and the flask was suspended in a thermostat at 20°. As soon as the temperature had been equalised, alcohol was added exactly to the mark and the flask with its contents weighed.

The water of the thermostat at 20° was made to circulate through a refractometer by a pump attached to a hot air motor. A small quantity of the solution was poured into the cylinder of the refractometer and observation made with a sodium light as usual.



In the case of the saturated solution, alcohol and an excess of benzophenone were introduced into two small bottles with well-fitted stoppers, tightly covered with thin caoutchouc cloth. One of the bottles was exposed to a somewhat higher temperature, and then both of them were fixed to the stirrer of the thermostat and allowed to rotate for a sufficient time to ensure saturation. Then a small quantity of the solution was transferred to the refractometer by means of a small tube, specially formed, as shown in the annexed figure.

The results obtained were as follows:

Table I.

No.	Benzophenone taken.	Volume of the solution.	Weight of the solution.	Angles observed.
1	0	—	—	61° 42′
2	0·7455	10·00	8·161	58° 36′
3	1·0000	10·00	8·247	57° 35′
4	1·2530	10·00	8·317	56° 33′
5	1·5004	10·00	8·396	55° 35′
6	1·7500	10·00	8·472	54° 39′
7	1·9998	10·00	8·541	53° 41′
8	2·2500	10·03	8·637	52° 44′
9	Saturated	—	—	52° 3′

From the above data, the following table has been obtained by calculation:

Table 2.

No.	Benzophenone		Δ.
	in 100 c.c. of the solution.	in 100 g. of the solution.	
2	7·455	9·136	3·10°
3	10·000*	12·126*	4·12°
4	12·530	15·065	5·15°
5	15·004	17·871	6·12°
6	17·500	20·656	7·05°
7	19·998*	23·414*	8·02°
8	22·433	26·050	8·97°
9	Saturated	Saturated	9·65°

Using the data marked *, the following equations are obtained:

For the amount of the solute in 100 c.c. of the solution,

$$0{\cdot}4225\,x - 0{\cdot}00108\,x^2 = \Delta$$

and

$$x = 195{\cdot}37 - \sqrt{\frac{41{\cdot}27 - \Delta}{0{\cdot}00108}};$$

and for the amount of the solute in 100 grams of the solution,

$$0{\cdot}3364\,x + 0{\cdot}000255\,x^2 = \Delta$$

and

$$x = \sqrt{\frac{111{\cdot}83 + \Delta}{0{\cdot}000255}} - 659{\cdot}05.$$

The following tables show the comparison of the results of the calculation by the empirical formulæ thus obtained with those directly calculated from the amounts of the substances used:

Table 3.

Benzophenone in 100 c.c. of the solution.

Exp.	Calc.	Diff.	Percent. diff.
7·455	7·48	+0·02	+0·2
10·000	—	—	—
12·530	12·60	+0·07	+0·6
15·004	15·06	+0·06	+0·4
17·500	17·47	−0·03	−0·2
19·998	—	—	—
22·433	22·52	+0·09	+0·4

Table 4.

Benzophenone in 100 grams of the solution.

Exp.	Calc.	Diff.	Percent. diff.
9·136	9·11	−0·03	−0·3
12·126	—	—	—
15·065	15·09	+0·02	+0·1
17·871	17·91	+0·04	+0·2
20·656	20·59	−0·07	−0·3
23·414	—	—	—
26·050	26·11	+0·06	+0·2

As is seen from the tables, the differences between the experimental and the calculated values, are less than one per cent. By means of the same empirical formulæ, the solubility of benzophenone in absolute alcohol specially used in the present experiments can be calculated as follows:

Benzophenone in 100 c.c. of the solution: 24·36
" " 100 grams " " " 28·05

And from the last data we have:

Benzophenone in 100 grams of the solvent: 39·00.

2. POTASSIUM CHLORIDE IN WATER.

In order to verify the empirical formula for the solutions of strong electrolytes, potassium chloride was taken and, proceeding as in the previous experiments, the following results were obtained:

Table 5.

No.	Potassium chloride taken.	Volume of the solution.	Weight of the solution.	Angles observed.
1	0	—	—	67° 32′
2	3·0038	20·08	21·844	63° 40′
3	4·4326	20·07	22·634	62° 8′
4	5·3590	20·03	23·094	61° 10′
5	Saturated	—	—	60° 33′

From the data of the last table, the following one was obtained:

Table 6.

No.	Potassium chloride		Δ.
	in 100 c.c. of the solution.	in 100 g. of the solution.	
2	14·959	13·751	3·87°
3	22·086	19·586	5·40°
4	26·755	23·205	6·37°
5	Saturated	Saturated	6·98°

By using the data of Experiments 2 and 4, the following equations are obtained:

For the amount of potassium chloride in 100 c.c. of the solution,

$$2{\cdot}844\,x - 0{\cdot}00174\,x^2 = \Delta$$

and

$$x = 81{\cdot}88 - \sqrt{\frac{11{\cdot}64 - \Delta}{0{\cdot}00174}}\,;$$

and for the amount of the solute in 100 grams of the solution,

$$0{\cdot}2910\,x - 0{\cdot}0072\,x^2 = \Delta$$

and

$$x = 201{\cdot}94 - \sqrt{\frac{29{\cdot}39 - \Delta}{0{\cdot}00072}}.$$

The results calculated by these formulæ are in satisfactory agreement with the experimental values, thus:

Table 7.

	Potassium chloride	
	in 100 c.c. of the solution.	in 100 g. of the solution.
Experiment	22·086	19·586
Calculated	21·92	19·49
Difference	−0·17	−0·10
Percent. difference ...	−0·8	−0·5

The solubility of potassium chloride in water at 20° is calculated as follows:

Potassium chloride in 100 c.c. of the solution: 29·97;
" " " 100 grams " " " 25·64;

And from the last data we have:

Potassium chloride in 100 grams of the selvent: 34·43,

and this is in good agreement with the value 34·4 estimated by Berkeley.[1]

3. ETHYL ETHER IN WATER.

Next, as an example of very volatile indifferent substances, ethyl ether was taken and its solubility in water was determined. The commercial pure ether was purified in the usual way, and the experiments were carried out as follows:

About 20 c.c. of water in a small flask of known weight, with a well-fitted stopper, was weighed, then a certain quantity of ether which is to be dissolved completely in the water, was added and again the flask was weighed. Two solutions of known composition thus prepared and a saturated solution at 20° were subjected to observation by the refractometer.

The results obtained are as follows:

Table 8.

	Water taken.	Ether added.	Ether in 100 g. of solution.	Angles observed.	Δ.
	—	0	0	67° 32′	—
I.	21·76	0·733	3·259	66° 58′	0·57°
	19·86	1·053	5·036	66° 38′	0·90°
II.	20·03	0·502	2·445	67° 8′	0·40°
	19·99	0·894	4·282	66° 48′	0·73°
	—	Saturated	Saturated	66° 13′	1·32°

From the data of the experiments of two series, the following equations are obtained respectively:

[1] Phil. Trans. **203A**, 207 (1904).

$$\text{I.}\quad \begin{cases} 0{\cdot}1644\,x + 0{\cdot}00285\,x^2 = \Delta, \\ x = \sqrt{\dfrac{2{\cdot}374 + \Delta}{0{\cdot}00285}} - 28{\cdot}88\,; \end{cases}$$

$$\text{II.}\quad \begin{cases} 0{\cdot}1535\,x + 0{\cdot}00414\,x^2 = \Delta, \\ x = \sqrt{\dfrac{1{\cdot}422 + \Delta}{0{\cdot}00414}} - 18{\cdot}53\,; \end{cases}$$

and it is calculated by these equations that the amount of ether in 100 grams of solution saturated at 20° is:

I. 7·13. II. 7·19. mean: 7·16.

From this data we have:

Ether in 100 grams of water: 7·7.

This result seems to be somewhat too high; but it may not be greatly different from the true value, if we may judge from the following data found in the literature of the subject:

Temperature.	Ether in 100 grams of water.	Observer.
20°	7·487	Schuncke.[1]
19°	7·494	Tolloczko.[2]
21°	6·948	
19°	7·17	Klobbie.[3]
19°	6·89	

CONCLUSION.

This method of solubility determination thus far examined, seems to give results so reliable as the usual methods when the solubility is not small. It is simple and practically convenient, and can be used when the usual methods fail.

April, 1907.

[1] Zeitschr. f. physik. Chem., **14**, 334 (1894).
[2] Ibid., **20**, 407 (1896).
[3] Ibid., **24**, 616 (1897).

Reaction between Carbonic Acid and Lead Acetate in an Aqueous Solution. II.

By

Jingoro Yamasaki.

In the author's previous communication on the same subject, it was remarked that the results obtained by him were not concordant with those by Bischof, and the disagreement was somewhat too great to be ascribed to a difference in the temperatures at which the experiments were conducted. Now, in the experiments carried out with a view to studying the influence of temperature on the reaction in question, no detail differed from those of the previous ones, except that the temperature is 15°. The results obtained were as follows:

Table I.

Initial equivalent concentration of lead acetate.	$\frac{1}{9.05}$n. sodium hydroxide needed for the neutralisation of the free acetic acid in 20 c.c. of the solution, after the reaction.			
	(a)	(b)	(c)	Mean.
2·0	101·88	101·63	—	101·76
0·4	54·39	—	54·36	54·38
0·2	27·91	27·96	27·91	27·93
0·15	21·31	21·36	21·31	21·32
0·10	14·41	14·66	14·46	14·48
0·05	7·18	7·18	7·28	7·21
0·0333	4·80	4·80	4·79	4·80

[1] These Memoirs I., 177.

From the data here given, the following table was obtained by calculation:

Table II.

Before the reaction.	After the reaction.		
Lead acetate.	Acetic acid.	Lead acetate.	$\frac{\text{Acetic acid.}}{\text{Lead acetate.}}$
2·0	1·1270	0·8730	1·28
0·4	0·3011	0·0989	3·04
0·2	0·1547	0·0453	3·41
0·15	0·1180	0·0320	3·69
0·10	0·0802	0·0198	4·04
0·05	0·0399	0·0101	3·96
0·0333	0·0266	0·0067	3·94

As is seen in the table, the ratio of acetic acid to lead acetate, in the solutions after the reaction, is somewhat greater than that in the former case, when the concentrations were comparatively high; but it becomes rather smaller, being practically equal, when the solutions are more diluted. The concentration at which it begins to cease exerting influence in this ratio, seems to show no remarkable degree of difference from what was found at 25°.

Dynamometer Car Experiments.
Part I.

By

Sakurô Tanabe and **Kakutarô Hori.**

The dynamometer car to be described in this paper is designed with a view to measuring draw-bar-pull, buffer-thrust, speed of train, vibration of train, etc., on the narrow-gauge (3 feet 6 inches) railways of Japan. The measuring appliances for the vibration being now in the stage of trial and improvement, our work has been so far carried out as to satisfy the preceding three requirements, which we intend to discuss in the present paper.

DESCRIPTION OF THE DYNAMOMETER CAR.

I. Description of the Car.

The car shown in figure 1, plate I, was built at the Osaka Locomotive Works. It has a total length of 18 feet 7 inches, and a wheel-base of 10 feet. In one-half of the room, we have arranged the measuring appliances, leaving the other half for future extension.

In figure 1, A. shows the recorder for draw-bar-pull; B. the recorder for buffer-thrust; and C. a Boyer's Railway Speed Recorder. The car is furnished with hand-brake and train-pipe, and is of nearly 6 tons weight, when ready for trial.

II. Description of the Dynamometrical Apparatus.

The dynamometrical apparatus, as stated before, gives :—

Pull of draw-bar, or train-resistance ;
Thrust on the buffer ;
Speed of train.

1° *Recording the Draw-bar-pull.*

In figure 3, plate II, the body of the draw-bar A. is extended beyond the principal cross-beam, where the piston B. is fixed to the bar with lock-nuts. To the same principal beam, the cylinder C. is bolted horizontally, to receive the piston B., and between these a strong helical spring is inserted. By this arrangement, any pull applied to the draw-bar compresses the spring proportionately to the force which is to be measured. This compression, or displacement of the draw-bar, is transmitted to the recording-pen K., hung from the horizontal bar, which is guided above the recorder shown in plate V, through the vertical rod E., the links F. and H., and the lever G., in figure 3, plate III.

The recording-pen K. describes a curve for the draw-bar-pull on a strip of paper, which travels over the rotating-drum of the recorder. The ordinates of the curve obtained are thus, at every moment, proportional to the pull exerted on the draw-bar.

To ensure accuracy of the measurements, the recorder is bolted rigidly to the bracket of the cylinder C., with the insertion of a metal plate I, between them ; thus eliminating errors caused by deflection of under-frames.

We have prepared two helical springs, shown in plate IV ; the one, in figure 14, for light service ; and the other, in figure 15, for heavy service.

2° *Construction of Recorder and Transmission of Train-motion to it.*

The motion is taken from one of the car-axles by means of an endless steel coil rope, to the first motion-spindle B. of the

recorder shown in figure 19, plate V. The rotation of spindle B. is then transmitted to the horizontal drum G., over which a strip of paper travels, through two pairs of worms B. and D., and worm-wheels C. and E., each having 32 teeth. The strip of paper is pressed by two rollers H., by means of levers and steel springs, against the rotating drum G., of 2½ inches diameter.

To draw the base-line on the moving strip of paper, another pen L. is clamped to the plate M. The position of mile-posts, of grades, and of curves along the railway, is marked by the same pen L. on the base-line by means of a pneumatic pipe and a pair of gun-balls which, when pressed at N. shift the pen L. sidewise.

3° *Recording the Buffer-thrust.*

In figure 30, plate VII, the tail-rod D., of the buffer A. is extended beyond the buffer-beam I, where a cotter is driven into the rod to prevent the buffer A. from going out of the casing B. By this arrangement, any thrust applied to the buffer-head compresses the spring C. proportionately to the force which is to be measured. The compression, or displacement of the buffer, is transmitted to the recording pen K., which is hung from the horizontal bar guided above the recorder, shown in plate V, through a vertical rod E., and a link F. in plate VII. The recording pen K. describes a curve, showing the buffer-thrust, on a strip of paper which travels over a rotating drum of the recorder. The ordinates of the curve thus obtained, are proportional at every moment to the thrust exerted on the buffer-head.

To ensure accuracy of measurement, the recorder is bolted rigidly to a metal plate which, bent over the buffer-beam, is inserted between the beam and the buffer-casing; thus eliminating errors which may be caused by the deflection of the under-frames.

4° *Construction of Recorder and Transmission of Train-motion to it.*

The construction of the recorder for buffer-thrust and transmis-

sion of movement from the car-axle, is in all respects similar to those for testing the draw-bar-pull. The base-line and the position of mile-posts, of grades, and of curves, is noted in like manner. The pneumatic pipes for the recorder of draw-bar-pull and buffer-thrust are all connected, so that a single compression of the gum-ball, N., deflects the three pens, L., simultaneously.

5° *Recording Speed of Train.*

Speed is measured by means of a Boyer's Railway Speed Recorder. Details of the construction of this recorder are given by the inventor in: "The Boyer's Railway Speed Recorder," from which we quote the following:

> "The principal parts of this machine consist of a rotary pump, a cylinder, and a piston. Oil is used as a circulating medium, the pump chambers and cylinder being entirely filled. While the machine is at rest, the piston to which the gauge wire and pencil are attached, is retained in its lowest position by two coil springs, but when given motion the pump produces a pressure of oil beneath the piston, causing it to rise to a point where an equilibrium is established between the pressure of oil and the tension of the springs, this point being determined by the speed at which the pump is moved; each thirty-second of an inch rise of the piston indicating a speed of one mile per hour. Moving around a drum in the upper part of the machine, at the rate of one-half inch to the mile, is a ribbon of paper, having thereon horizontal and vertical lines, each horizontal line, from the base or zero line, representing five miles per hour, and each vertical line a mile post along the road."

To ensure accuracy of measurement, we read the time, in decimals of a second, at successive quarter-mile posts by means of an accurate stop-watch and, comparing the results thus obtained with the curve of speed, correct the error of the scale.

6° *Transmission of Train-motion to Speed-recorder.*

The motion is taken from one of the axles of the car, by means of an endless rope of steel coil, to the first motion-spindle of the recorder.

TRIAL RUN OF THE DYNAMOMETER CAR.

Up to the present time, trials have been made on the following mentioned dates and over the lines named:—

Date.			Section.		Miles.	
Jan.	24	1904	Kyôto—Baba	(Tôkaido Railway Line)	10·1	
			Baba—Kyôto		10·1	
						20·2 miles.
May	5	1904	Kyôto—Baba	(Tôkaido Railway Line)	10·1	
			Baba—Kyôto		10·1	
,,	6	,,	,, ,,		10·1	
			,, ,,		10·1	
,,	7	,,	,, ,,		10·1	
			,, ,,		10·1	
,,	8	,,	,, ,,		10·1	
			,, ,,		10·1	
						80·8 miles.
July	17	1904	Numazu—Yamakita	(Tôkaido Railway Line)	27·5	
			Yamakita—Numazu		27·5	
,,	18	,,	,, ,,		27·5	
			,, ,,		27·5	
,,	19	,,	,, ,,		27·5	
			,, ,,		27·5	
,,	20	,,	,, ,,		27·5	
			,, ,,		27·5	
,,	21	,,	Numazu—Nagoya		149·0	
,,	22	,,	Nagoya—Kyôto		94·7	
						463·7 miles.

Date.			Section.		Miles.
Jan.	21	1905	Numazu—Yamakita	(Tôkaido Railway Line)	27·5
			Yamakita—Numazu		27·5
„	22	„	„ „		27·5
			„ „		27·5
„	23	„	„ „		27·5
			„ „		27·5
„	24	„	Numazu—Nagoya		149·0
„	25	„	Nagoya—Kyôto		94·7
					408·7 miles.
July	17	1905	Kyôto—Nara	(Kwansai Railway Line)	26·0
			Nara—Osaka		25·5
„	18	„	Osaka—Nara—Nagoya		106·8
„	19	„	Nagoya—Nara—Osaka		106·8
„	20	„	Osaka—Nara—Nagoya		106·8
„	21	„	Nagoya—Nara—Osaka		106·8
			Osaka—Nara		25·5
			Nara—Kyôto		26·0
					530·2 miles.
May	17	1906	Kyôto—Nagoya	(Tôkaido and Hokuriku Railway Line)	94·7
„	23	„	Nagoya—Maibara		
			Maibara—Kanazawa		161·7
„	24	„	Kanazawa—Toyama		
			Toyama—Fukui		123·5
„	25	„	Fukui—Maibara		
			Maibara—Kyôto		113·6
					490·5 miles.

Thus far, the total trial runs amount to about 2,000 miles, and before proceeding further in the trials, we purpose publishing the results of the accomplished trials, one after another.

I. Trial-Run between Numazu and Yamakita. (January 22nd, 1905).

1° *Particulars of Engine and Train.*

The engine under trial was a six-wheel coupled tank engine, built at the Kôbe Works, Imperial Government Railway; shown in figure 37, plate IX. The cylinders, placed outside, have a diameter of 16 inches and a stroke of 24 inches. The diameter of the coupled driving-wheels is 4 feet 1 inch; that of the radial-wheels 3 feet 2 inches: the rigid wheel-base is 12 feet 6 inches, and the total wheel-base is 27 feet 3 inches. The engine weighs, in working order, 51 tons. The boiler has a total heating surface of 952 square feet and a grate area of 15·4 square feet. The valve setting is shown in table I, plate IX.

The engine hauled a train, shown in figure 38, composed of 10 covered wagons, 2 open wagons, a brake-van, and a dynamometer-car, and the train weighed 134·375 tons of 2240 lbs., of which the load of 128·425 tons was hauled through the dynamometrical spring.

2° *Results of the Trial.*

The engine test, made by Mr. Y. Aoyama, Engineer of the Imperial Government Railway, gave the results shown in table III, plate IX. The indicator diagrams of the engine, taken at the positions marked from 1 to 13 in figure 41, plate IX, are shown in plates from XII to XVII.

The curves of speed, of draw-bar-pull, and of buffer-thrust, obtained by means of the recorders, are shown in figure 42, plate X, and in figure 43, plate XI.

The report from the Numazu Meteorological Observatory is shown in table V, plate XII.

II. Trial-Run between Kyôto and Baba. (January 24th, 1904).

1° *Particulars of Engine and Train.*

The engine under trial was a six-wheel coupled Bissel truck tender engine, built at the Kôbe Works of the Imperial Government Railway. The cylinders, placed outside, have a diameter of 17 inches, and a stroke of 22 inches. The diameter of the coupled driving-wheels is 4 feet 1 inch; that of the leading-wheels is 2 feet 7 inches; the rigid wheel-base is 12 feet 6 inches, and the total length of the engine is 46 feet 11¾ inches. The engine weighs, in working order, 41 tons 8 cwt., and the tender 16 tons 8 cwt. The boiler has a total heating surface of 965 square feet and a grate area of 15·77 square feet.

The engine hauled, through the dynamometrical spring, the following loads:—

Up train

Kyôto—Inari:

A load of 128·4 tons, consisting of 9 covered wagons, 4 open wagons, and a brake-van.

Inari—Baba:

A load of 86·0 tons, consisting of 9 covered wagons and a brake-van.

Down train

Baba—Otani:

A load of 83·7 tons, consisting of 5 covered wagons, 4 open wagons, and a brake-van.

Otani—Kyôto:

A load of 77·1 tons, consisting of 5 covered wagons, 4 open wagons, and a brake-van.

2° *Results of the Trial.*

The curves of speed, of draw-bar-pull, of buffer-thrust, and of the vibration of the car, recorded by the vibration recorder,

shown in figure 48, are shown in figure 44 and figure 45, plate XIX.

III. Trial-Run between Osaka and Nagoya, along the Kwansai Railway. (July 18th and 20th, 1905).

1° *Particulars of Engine and Train.*

The engine under trial was a six-wheel coupled Bissel truck tender engine, belonging to the Kwansai Railway, built by Dubs and Company, England. The cylinders, placed outside, have a diameter of 17 inches and a stroke of 22 inches. The diameter of the coupled driving-wheels is 4 feet, that of the leading-wheels 2 feet 6 inches; the rigid wheel-base is 12 feet 6 inches, and the total length of the engine is 38 feet 6 inches. The engine weighs, in working order, 40·5 tons, and the tender 23 tons. The boiler has a total heating surface of 991·7 square feet and a grate area of 16·6 square feet.

The engine hauled, through the dynamometrical spring, a load of 100·6 tons on the 18th and of 101·6 tons on the 20th; both trains composed of 5 bogie passenger cars.

2° *Results of the Trial.*

The curves of speed and of draw-bar-pull, taken during the trial on the 18th, are shown in figure 46, plate XX. The curves of speed and of draw-bar-pull, taken during the trial on the 20th, are shown in figure 47, plate XXI.

PLATE I

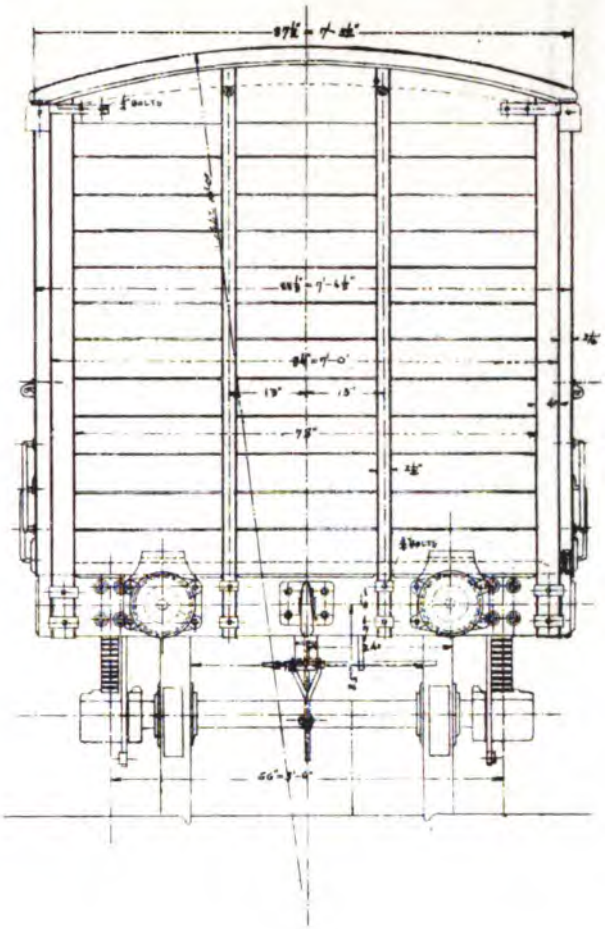


FIG 2

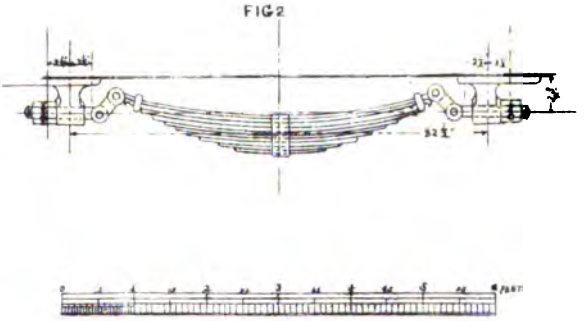
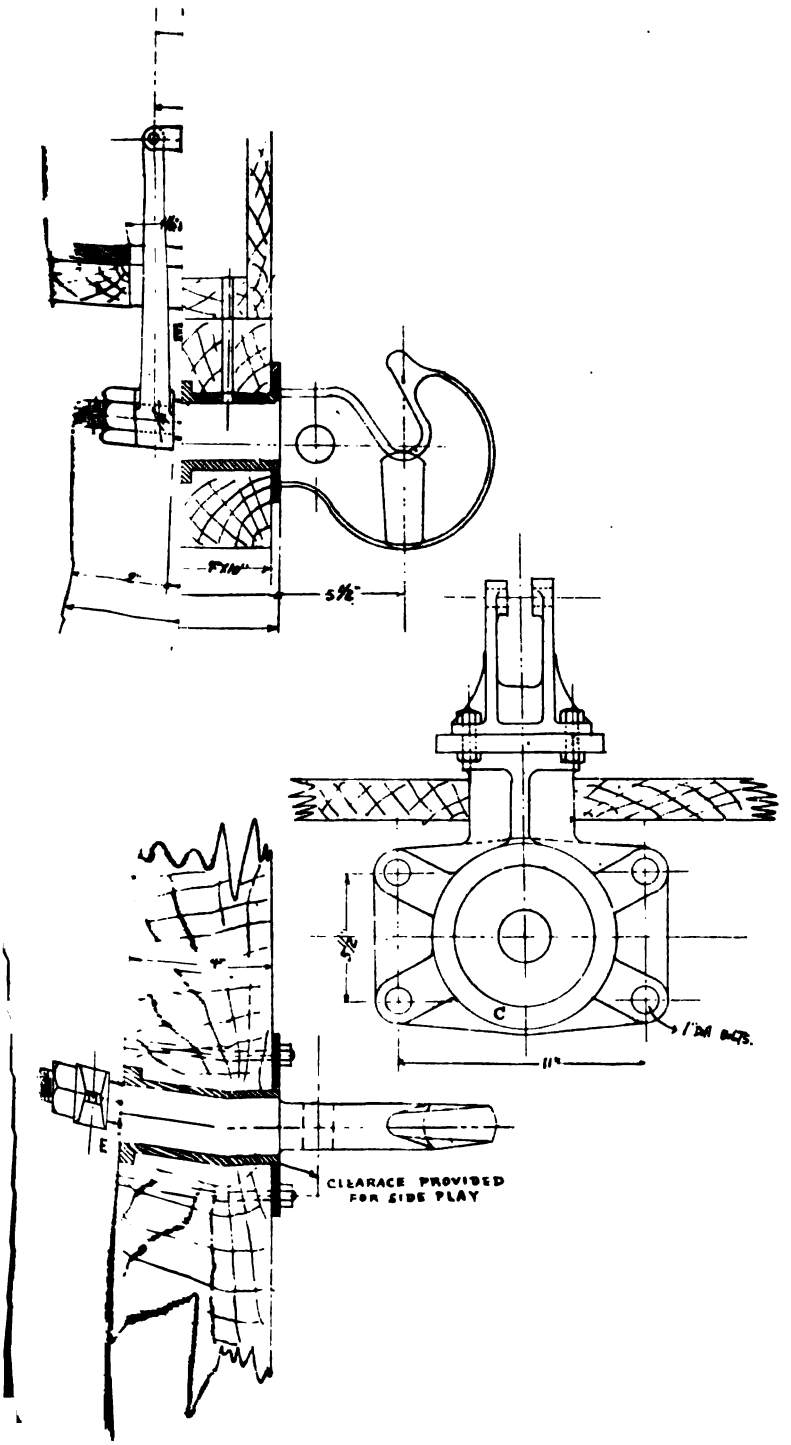


PLATE II



DESCRIPTION OF THE DYNA

DETA

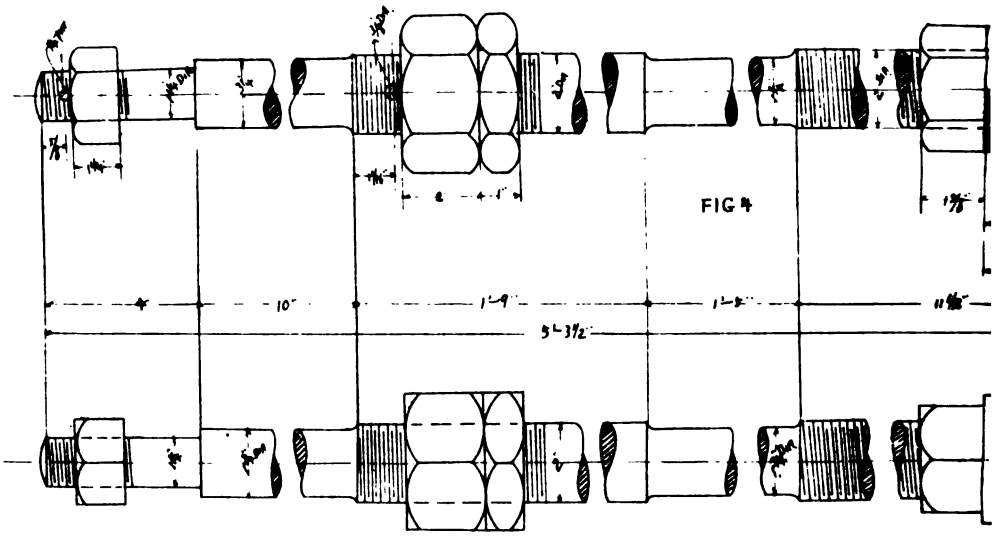


FIG 4

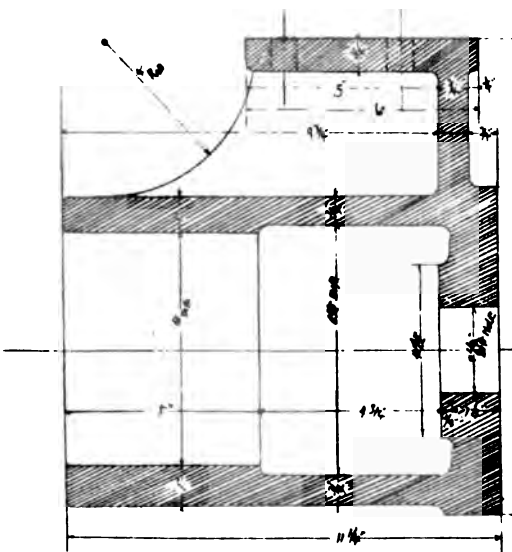


FIG 6

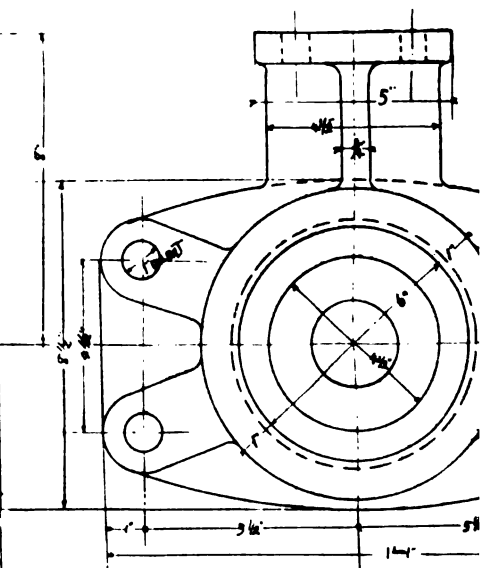
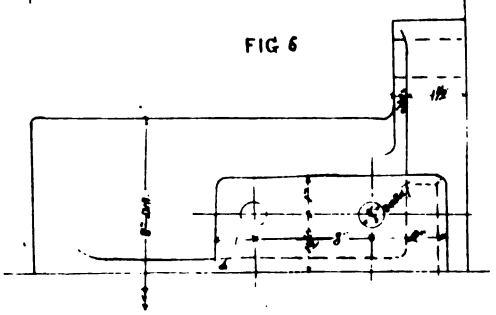
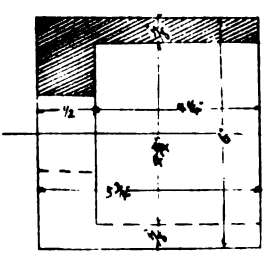
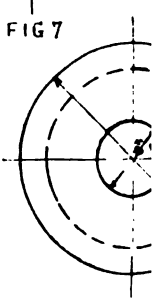


FIG 7



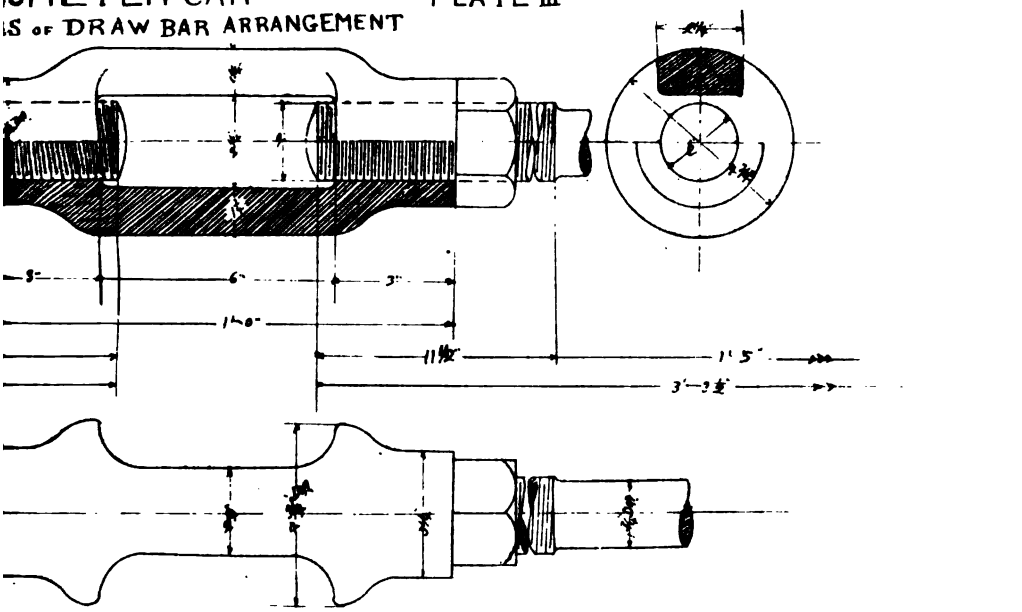




OMETER CAR

PLATE III

S OF DRAW BAR ARRANGEMENT



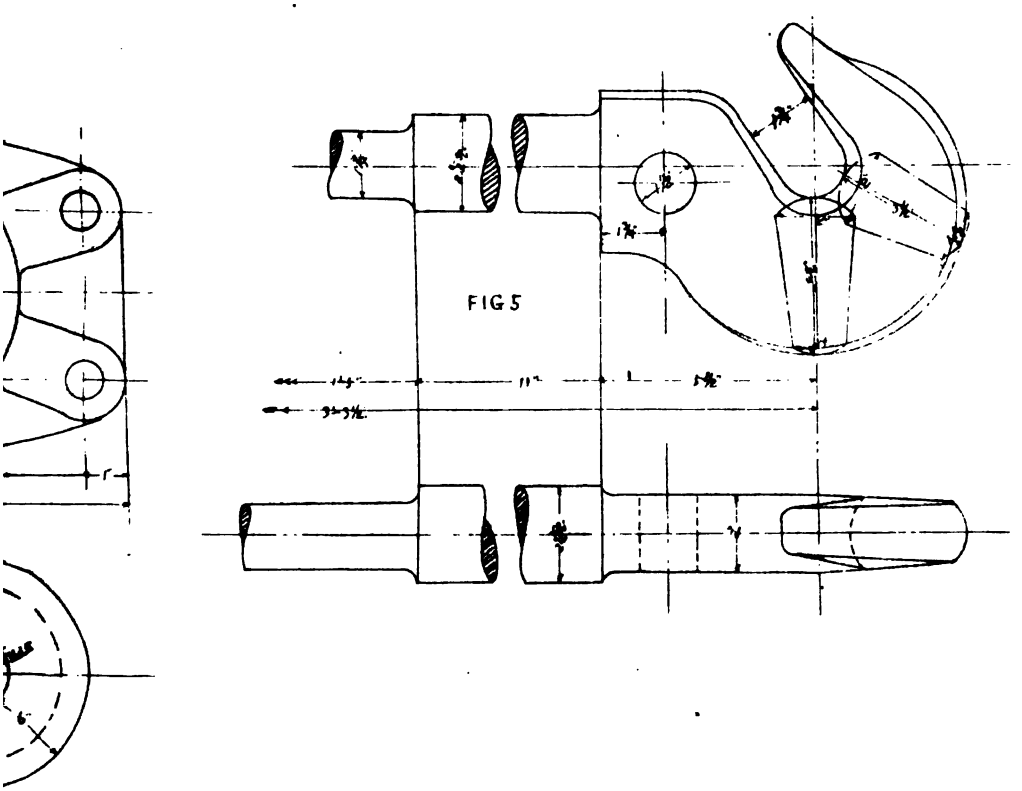


FIG 5

DESCRIPTION OF THE DYNAM

DETAILS OF DRAW

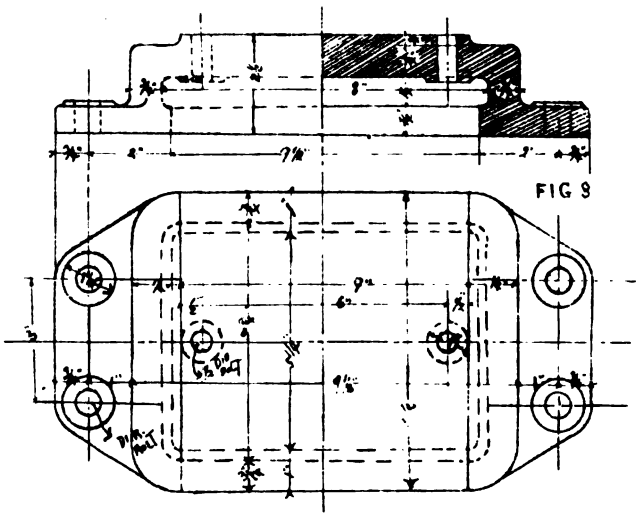


FIG 8

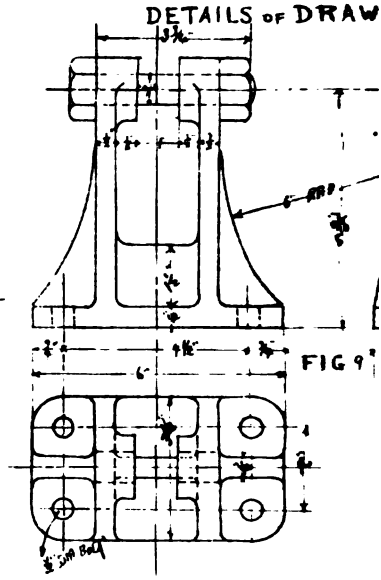


FIG 9

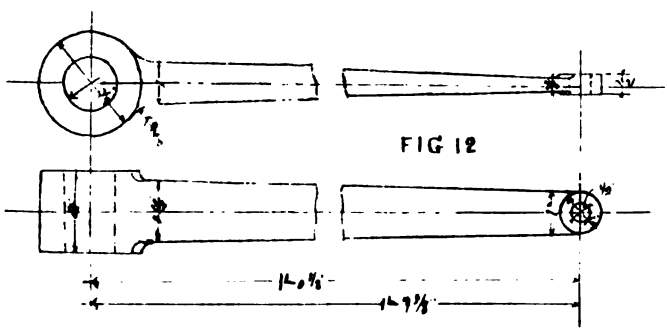
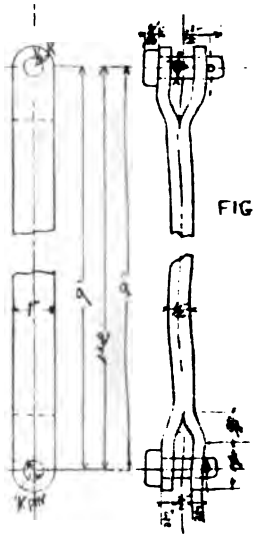


FIG 12



FIG

FIG 16

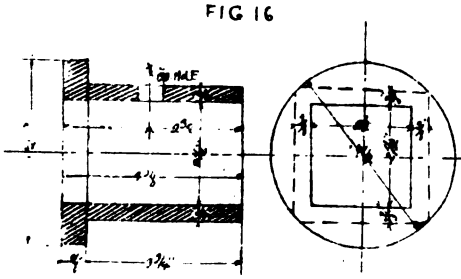
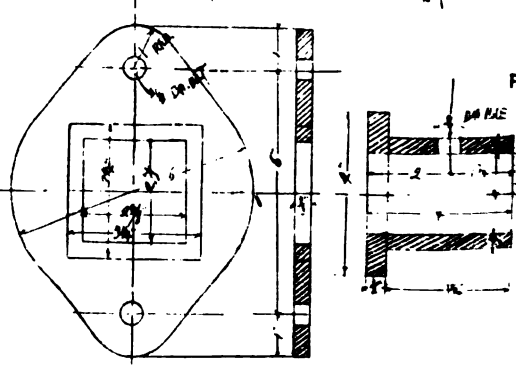
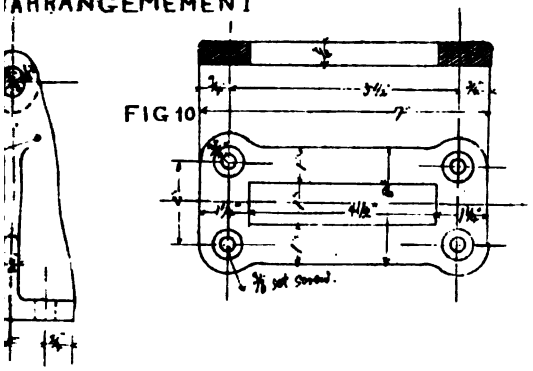


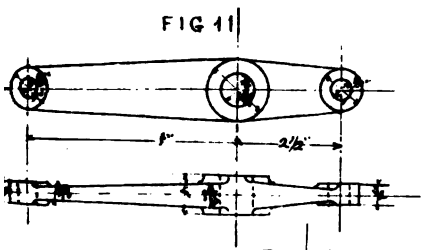
FIG 17

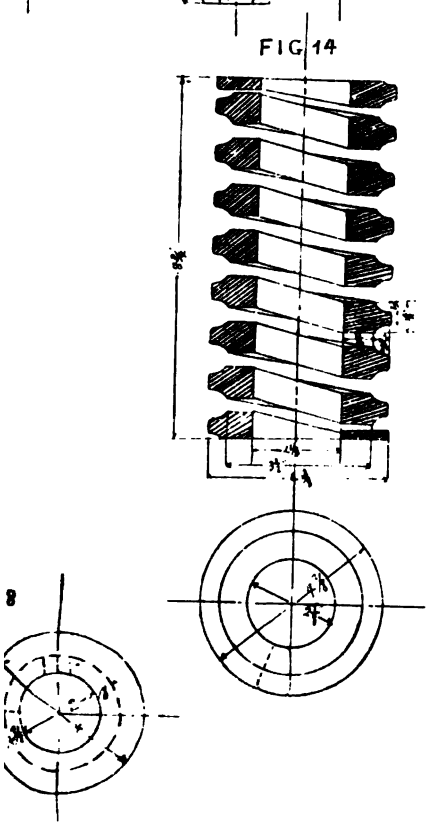


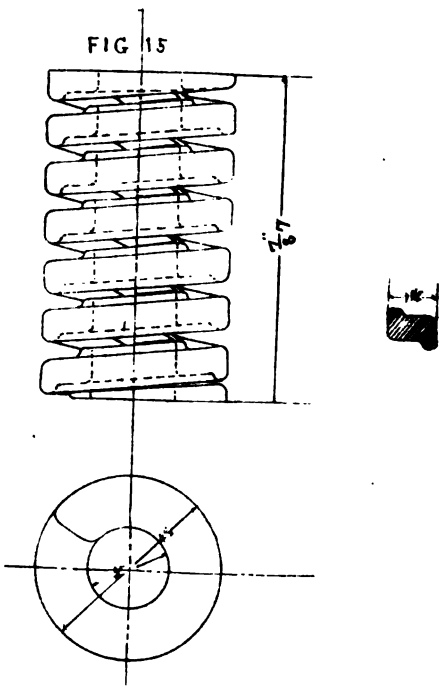
ETER CAR
ARRANGEMEMENT

PLATE IV



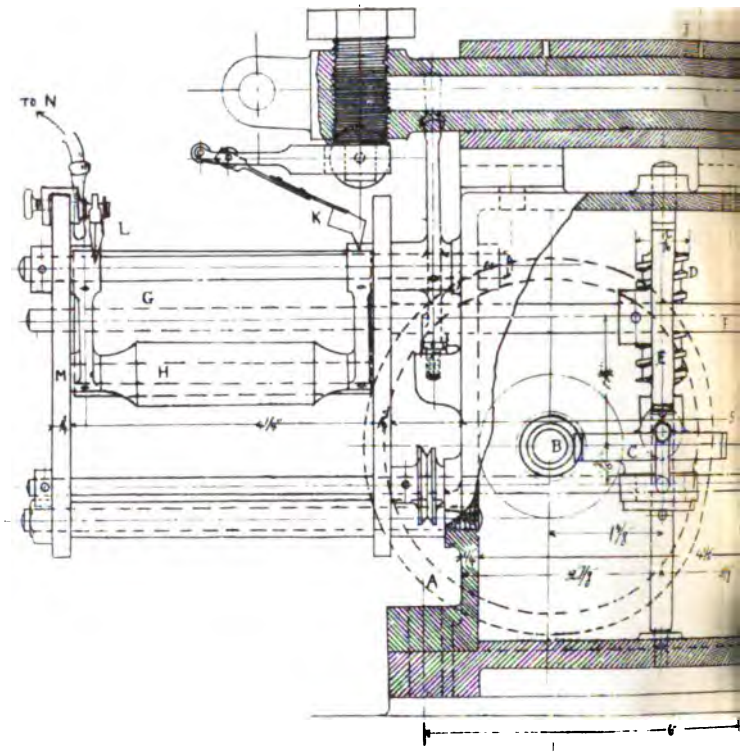


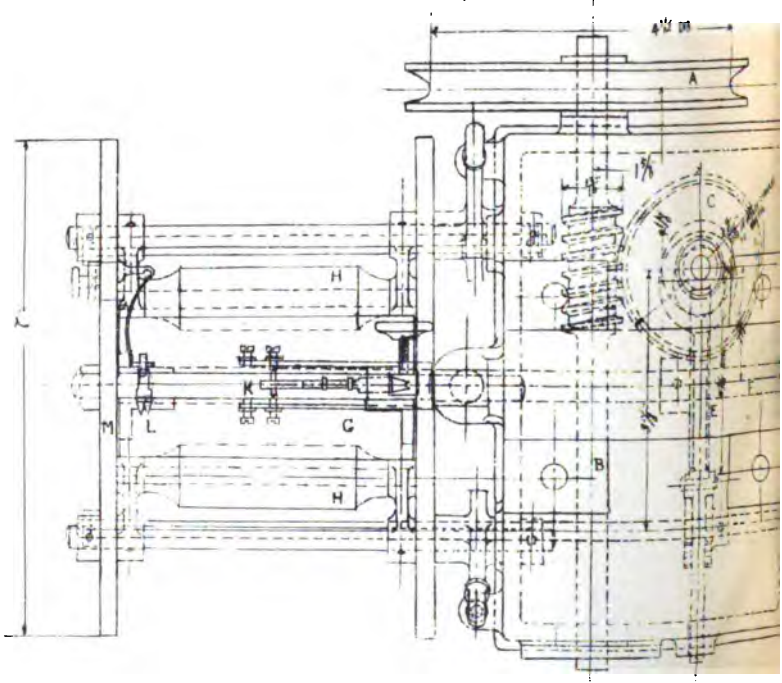




8

DESCRIPTION OF THE RECOR





NAMOMETER CAR
OF DRAW BAR PULL AND BUFFER THRUST

PLATE V

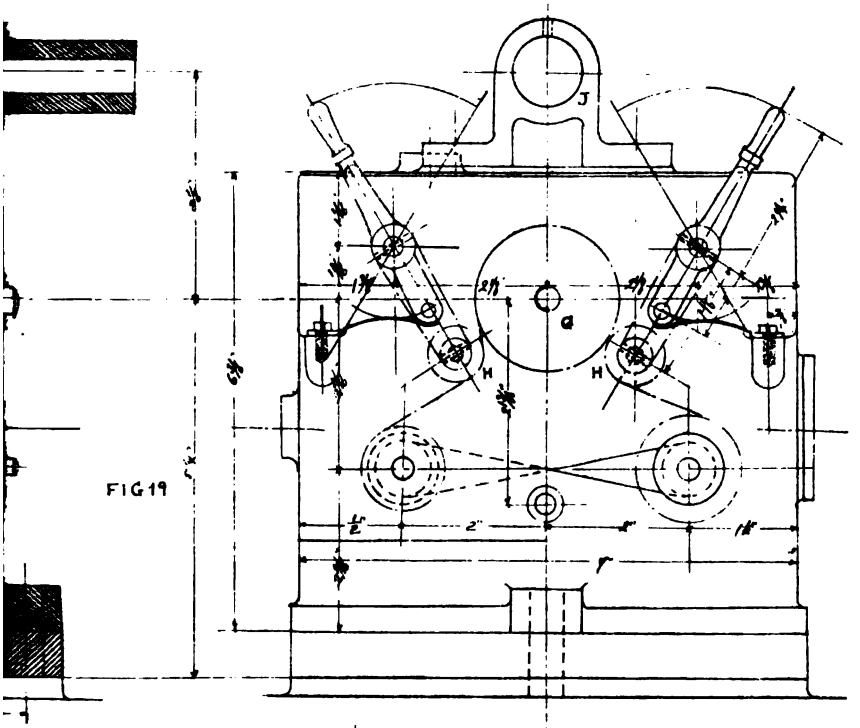


FIG 19

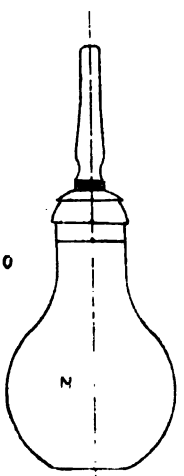
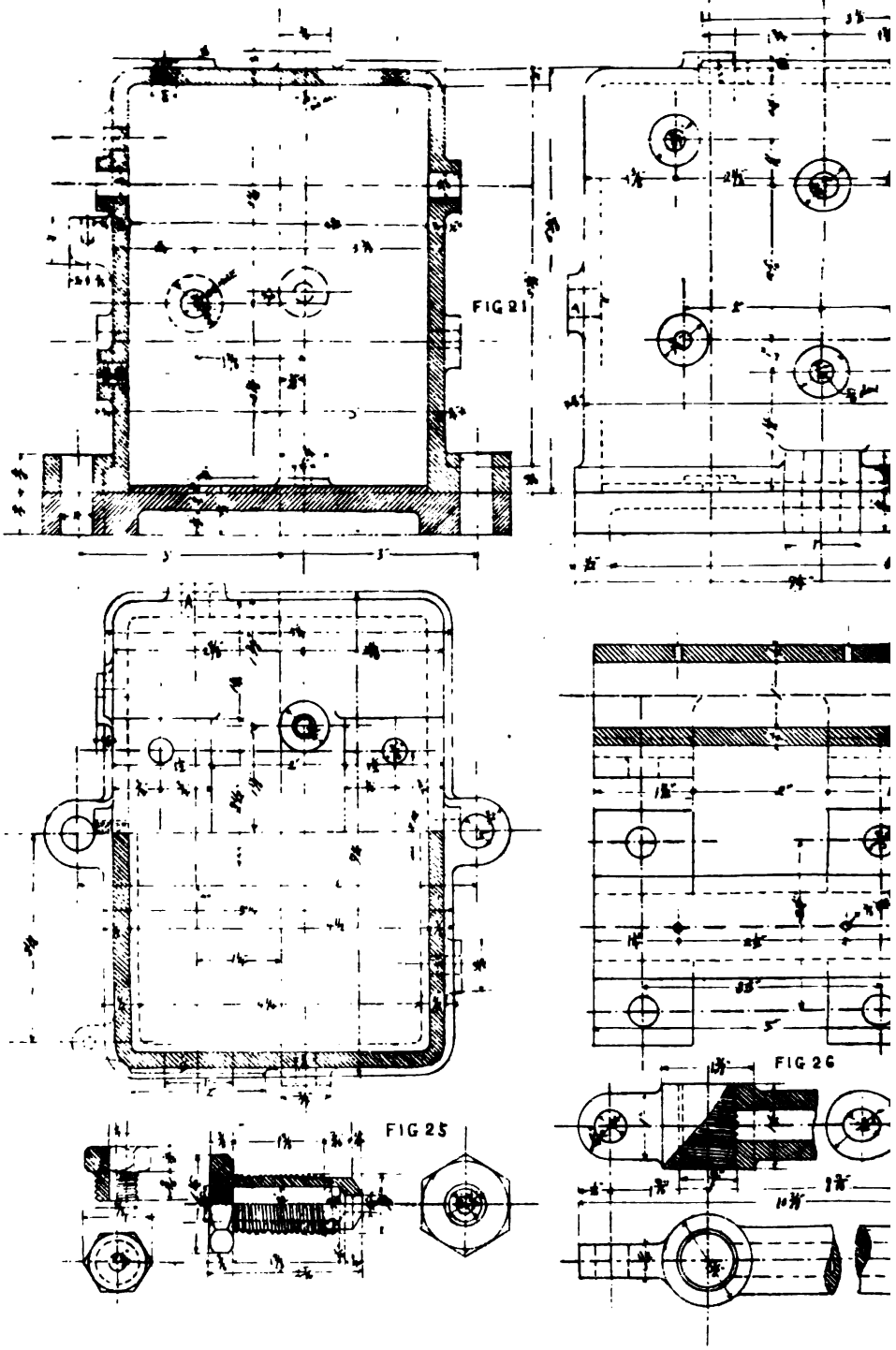


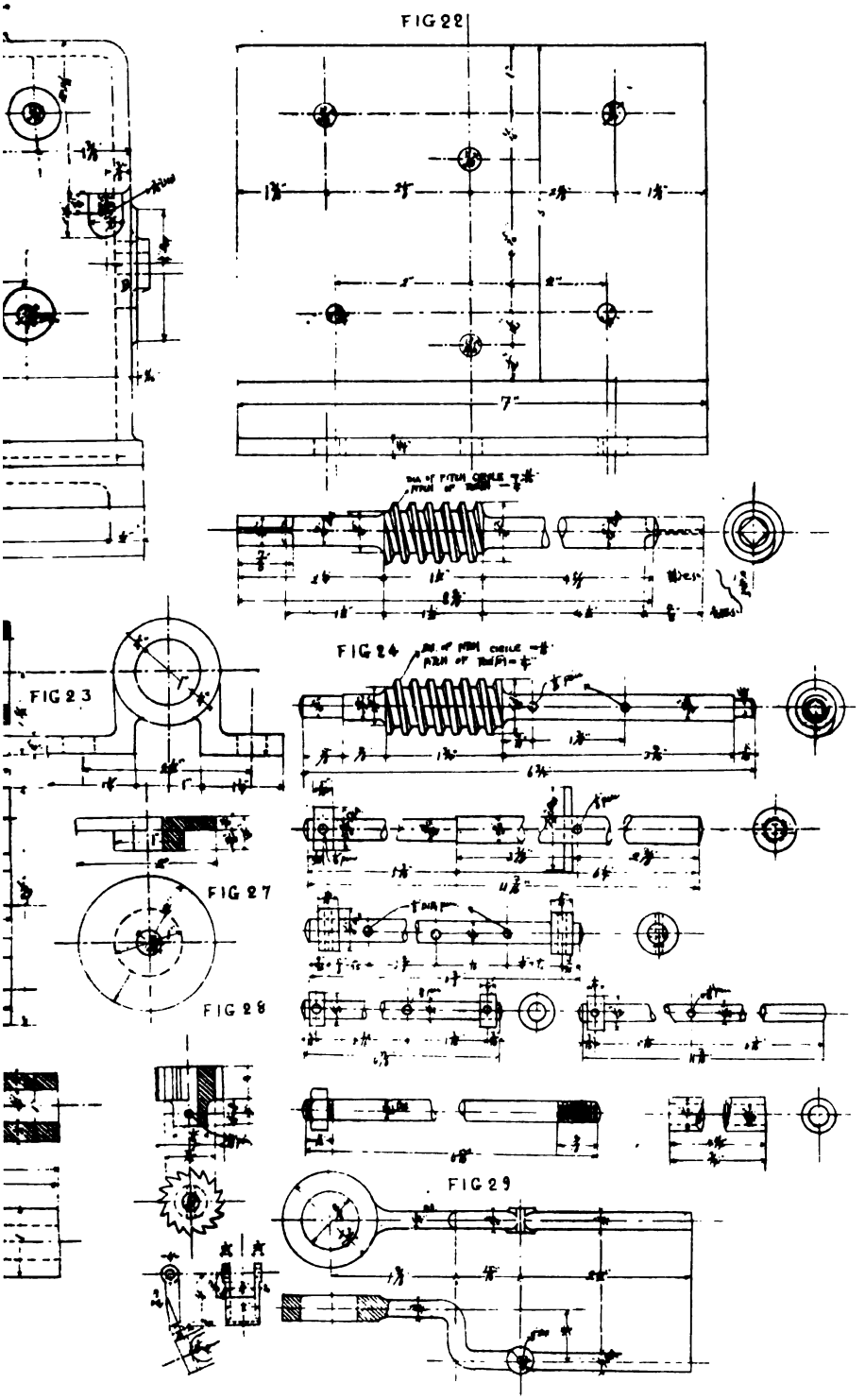
FIG 20

DESCRIPTION OF THE DYN



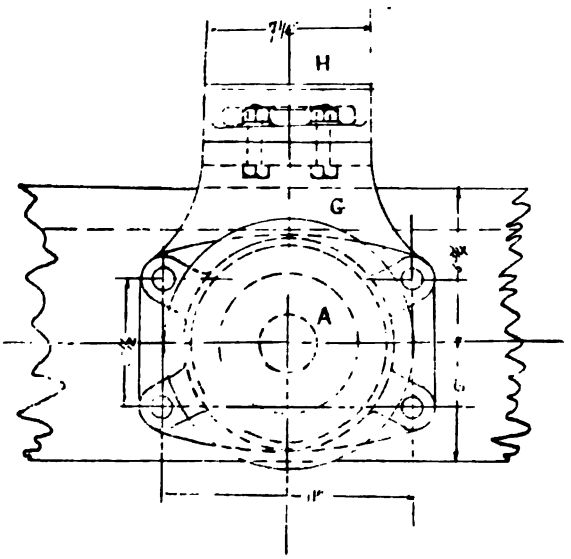
)METER CAR PLATE VI

DETAILS OF RECORDER



DESCRIPTION OF THE DYN

ARRANGEMENT FOR
RECORDING BUFFER THRUST



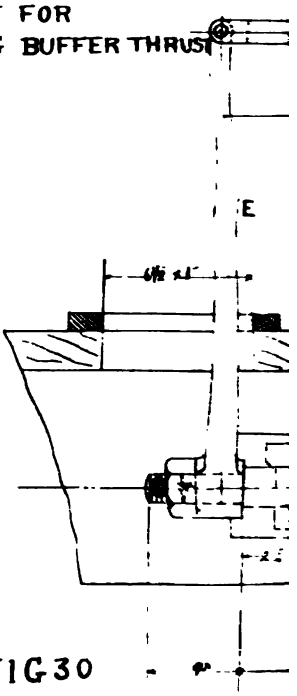
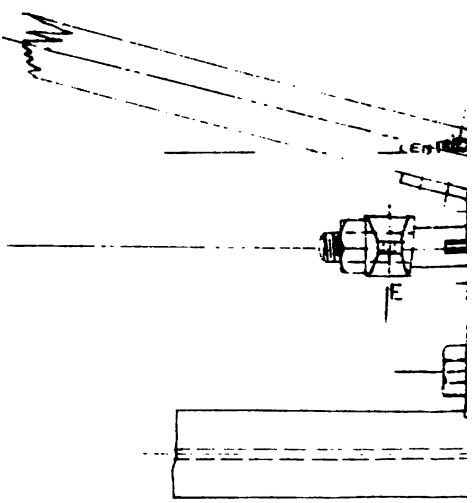
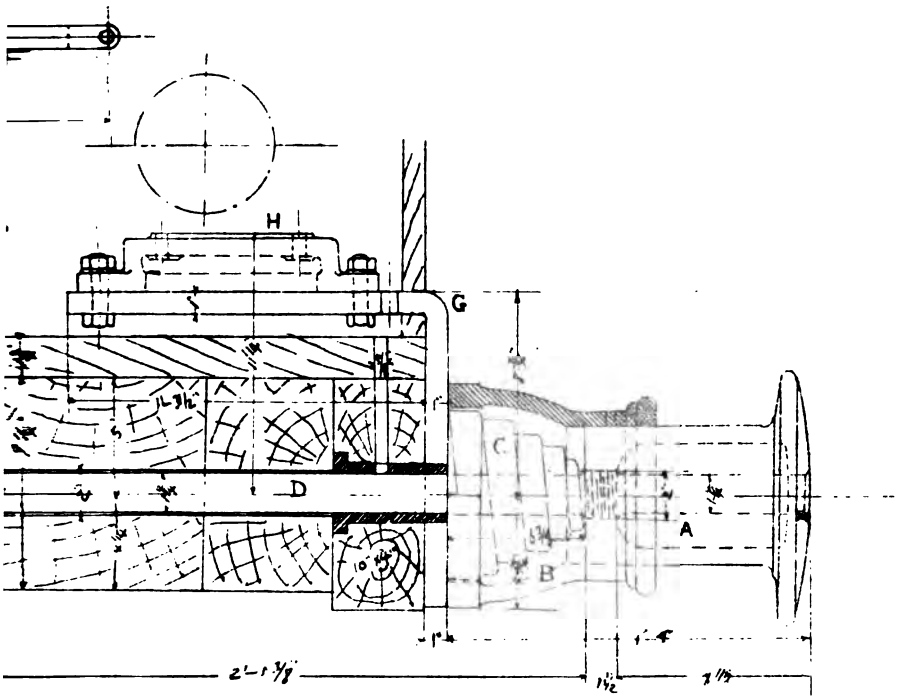
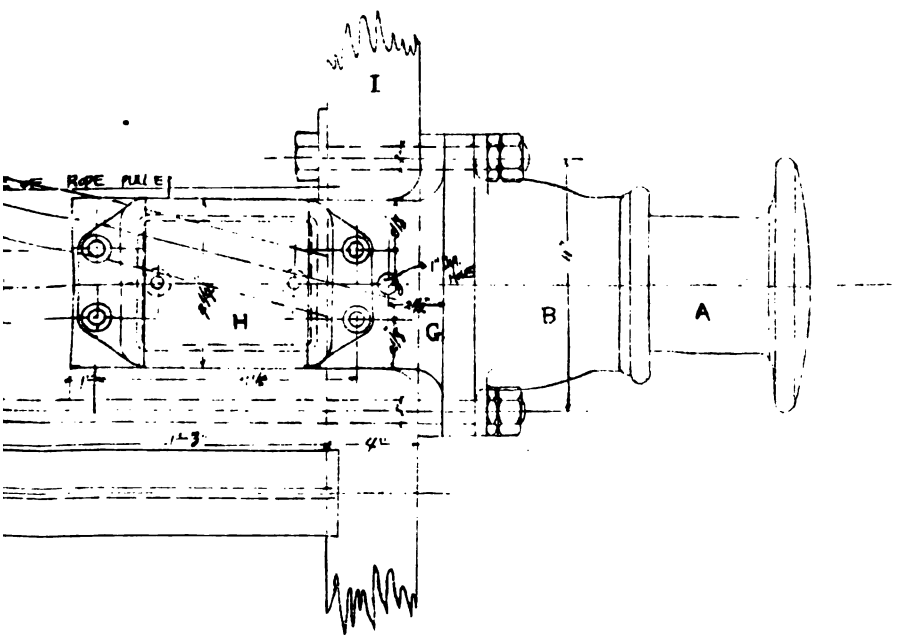


FIG30



OMETER CAR PLATE VII





DESCRIPTION OF

DETAILS

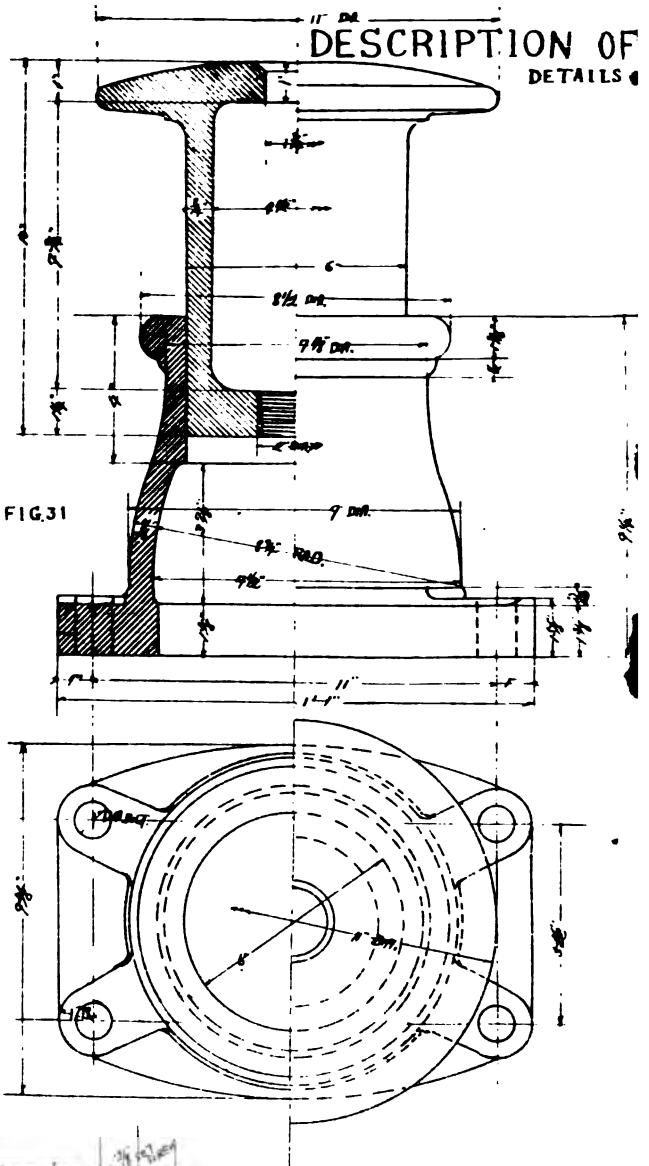


FIG.31

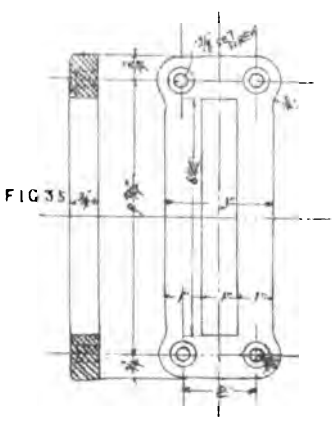


FIG.35

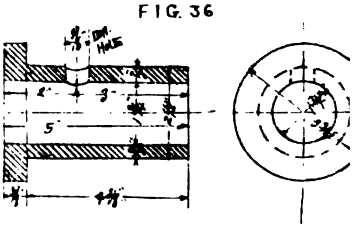


FIG. 36

THE DYNAMOMETER CAR

PLATE VIII

BUFFER ARRANGEMENT

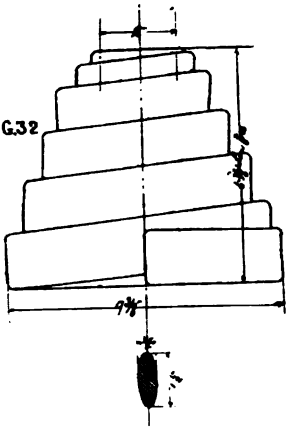
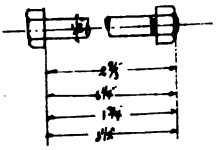


FIG 32



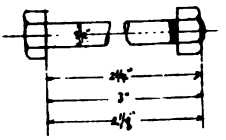
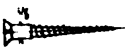
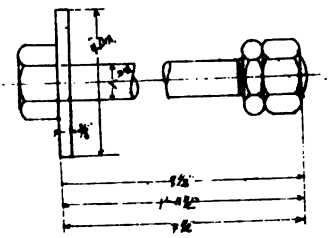


FIG 33





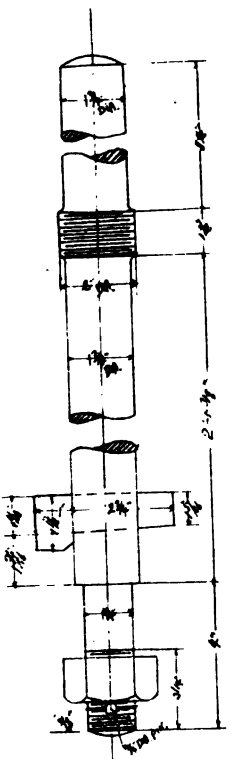
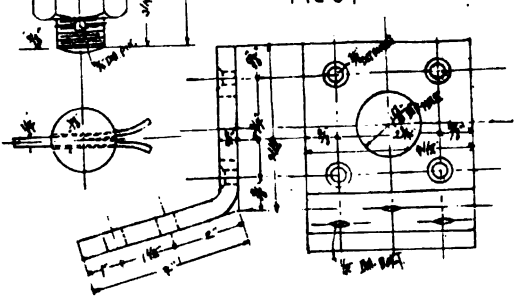


FIG 34

FIG 37



THE TRIAL RUN OF THI

FIG 38

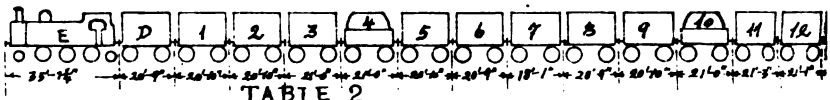


TABLE 2

	KINDS	WEIGHT (EMPTY) in KINS	WEIGHT (LOADED) in KINS
E	ENGINE		
D	DYN CAR		10000
1	COVERED WAGON	8700	8700
2	" "	8450	17500
3	" "	8378	17700
4	OPEN WAGON	7371	18800
5	COVERED WAGON	8191	18000
6	" "	7619	20500
7	" "	8381	19250
8	" "	8106	17600
9	" "	8050	15100
10	OPEN WAGON	7056	20000
11	COVERED WAGON	9991	21800
12	" "	9156	8800
13	" "		12000
TOTAL			225750

1680 KINS = 2240 POUNDS = 1 TON

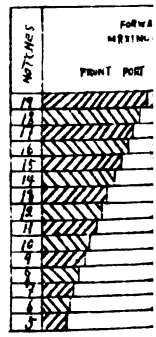
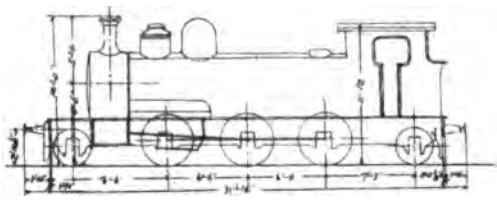


FIG 39



CYLINDERS	16" x 24"	TANK CAPACITY	1310 GAL
DIA OF RADIAL WHEELS	3'-2"	COAL	34 LB
" COUPLED	4'-1"	WEIGHT ON RADIAL WHEEL (FRONT)	6T 2C 1Q
RIGID WHEEL BASE	12'-6"	COUPLED	12. 6. 3
TOTAL	27'-3"	DRIVING	12. 13. 1
" LENGTH OF ENGINE	31'-1½"	COUPLED (HIND)	12. 17. 0
HEATING SURFACE IN TUBES	911 FT	RADIAL	6
" FIRE BOX	890	WORKING STEAM PRESSURE	190
GRATE AREA	154	WEIGHT OF ENGINE IN WORKING ORDER	31T 2C 2Q

FIG 40

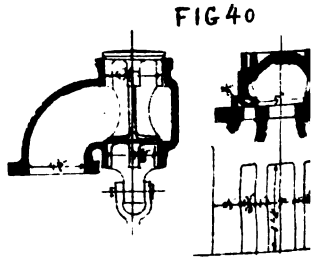


TABLE 3

	1ST TRIAL	2ND TRIAL	3RD TRIAL
DATE	21ST JANUARY 05	22ND "	23RD "
SECTION	[illegible]	— " —	— " —
TOTAL MILEAGE	15.3 M	— " —	— " —
LOAD HAULED	127 TON	124 TON	149.7 TON
COAL CONSUMED	2133.3 LBS	1826.6 LBS	2486.6 LBS
WATER CONSUMED	1448.44 GAL	1303.54 GAL.	1948.695 GAL.
WATER EVAPORATED PER LB. OF COAL	6.79 LBS	9.13 LBS.	7. LBS
FUEL	"OCHI" BITUMINOUS COAL	— " —	— " —
THEORETICAL EVAPORATIVE			
POWER OF COAL USED			
OVERFLOW FROM INJECTOR	16.6 GAL	12.8 GAL.	24.9 GAL.
WEATHER	CLOUDY	RAINY	CLEAR
AVERAGE GRADIENTS	9 in 500 UP	— " —	— " —
WATER CONSUMED PER TON MILE	.745 GAL.	.68 GAL.	.76 GAL.
COAL CONSUMED PER TON MILE	1.09 LBS.	.96 LBS.	1.08 LBS.
NUMBER OF CARS	13	14	16
RUNNING TIME	1H 25M	1H 24M	2H 7M
BOILER PRESSURE	150 LBS	— " —	— " —
TEMPERATURE OF FEED WATER	19°	15°	15° 47°

	WATER PER [illegible]	TON MILE LOAD [illegible]	COAL PER TON [illegible]	MILE LOAD [illegible]
1ST TRIAL	.513 GAL.	.89 GAL	8 LBS	1.28 LBS.
2ND "	.516 "	.79 "	.82 "	1.05 "
3RD "	.485 "	.937 "	.844 "	1.23 "

DYNAMOMETER CAR PLATE IX

JAN. 22. 1905 FROM NUMAZU TO YAMAKITA.

TABLE 1
VALVE SETTING FOR B7 CLASS.

Reverse Opening	Backward Gear Maximum Opening		Cut Off Percentages				Release Percentages				Lead	
			Forward		Backward		Forward		Backward			
Back Port	Front Port	Back Port	F. P.	B. P.	F. P.	B. P.	F. P.	B. P.	F. P.	B. P.	F. P.	B. P.
			78	80	74	76	93	94	94	[illegible]	41	38
			77	78	76	79	92	93	93	91	36	43
			74	76	75	77	93	92	92	92	35	38
			73	77	71	74	91	92	91	92	37	36
			70	70	68	67	90	90	90	89	38	36
			69	67	69	69	89	89	89	89	36	36
			65	62	65	64	88	88	87	87	36	35
			63	60	63	63	87	87	86	86	35	35
			58	58	59	59	85	85	85	85	35	35
			53	52	55	54	84	84	84	83	35	35
			49	47	51	49	81	81	81	79	35	35
			45	43	46	47	80	79	78	77	35	35
			42	37	40	36	77	76	75	75	35	37
			35	33	34	34	74	73	73	73	35	35
			31	28	26	27	71	70	71	69	35	35

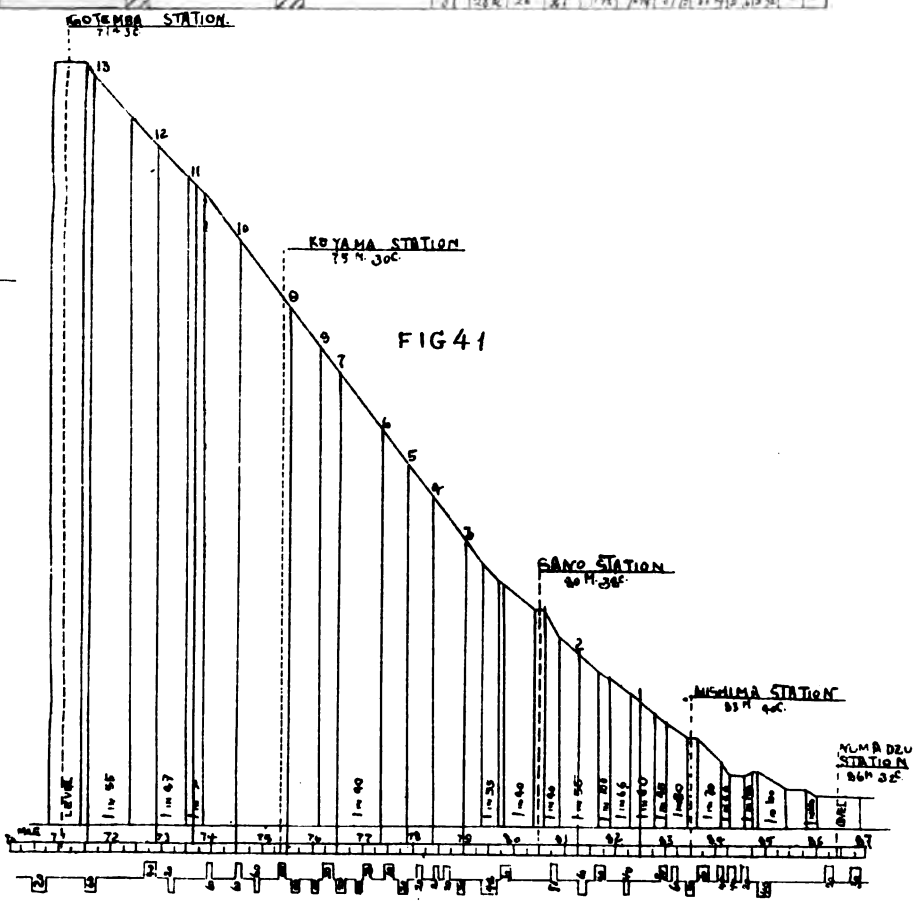


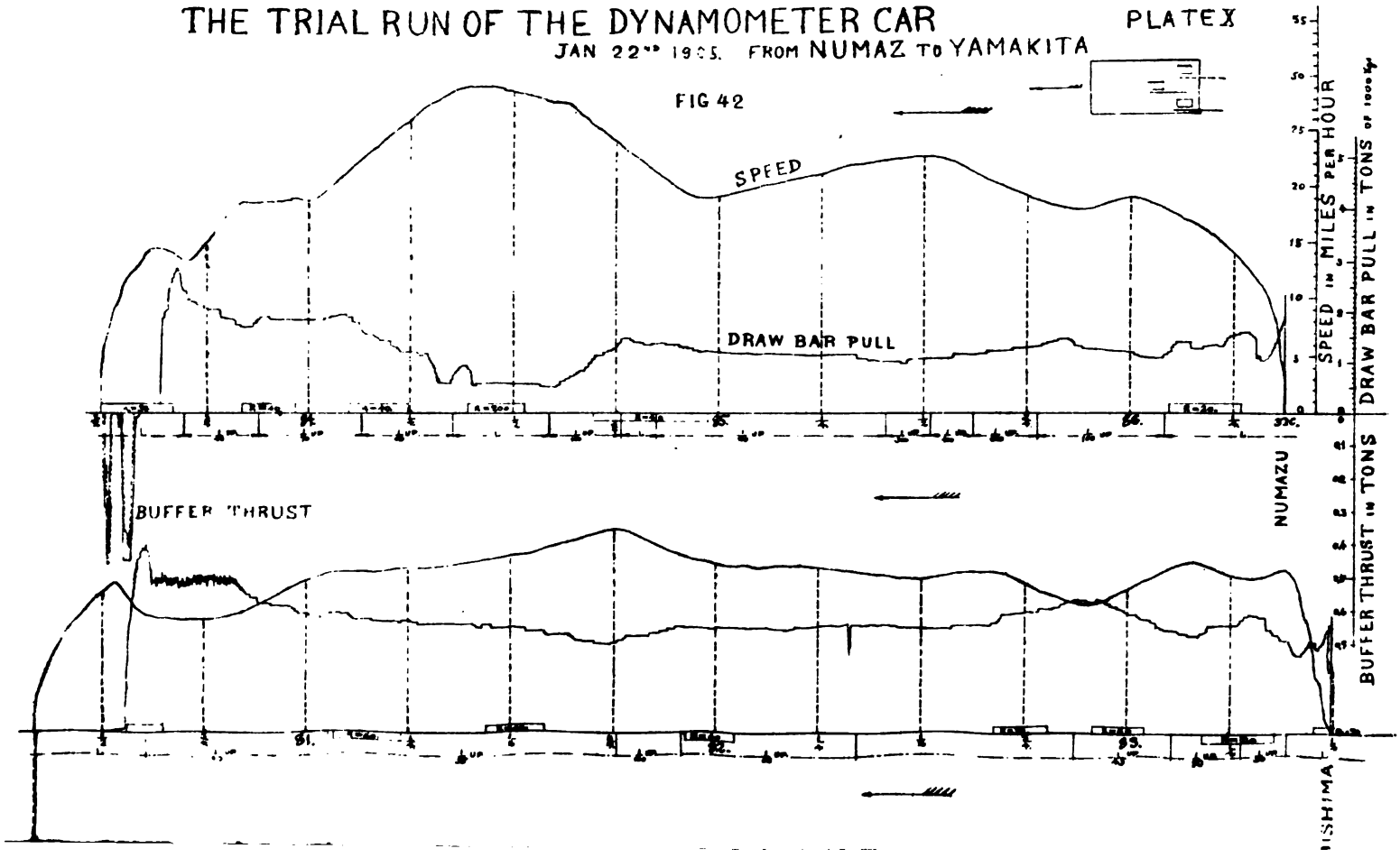
FIG 41

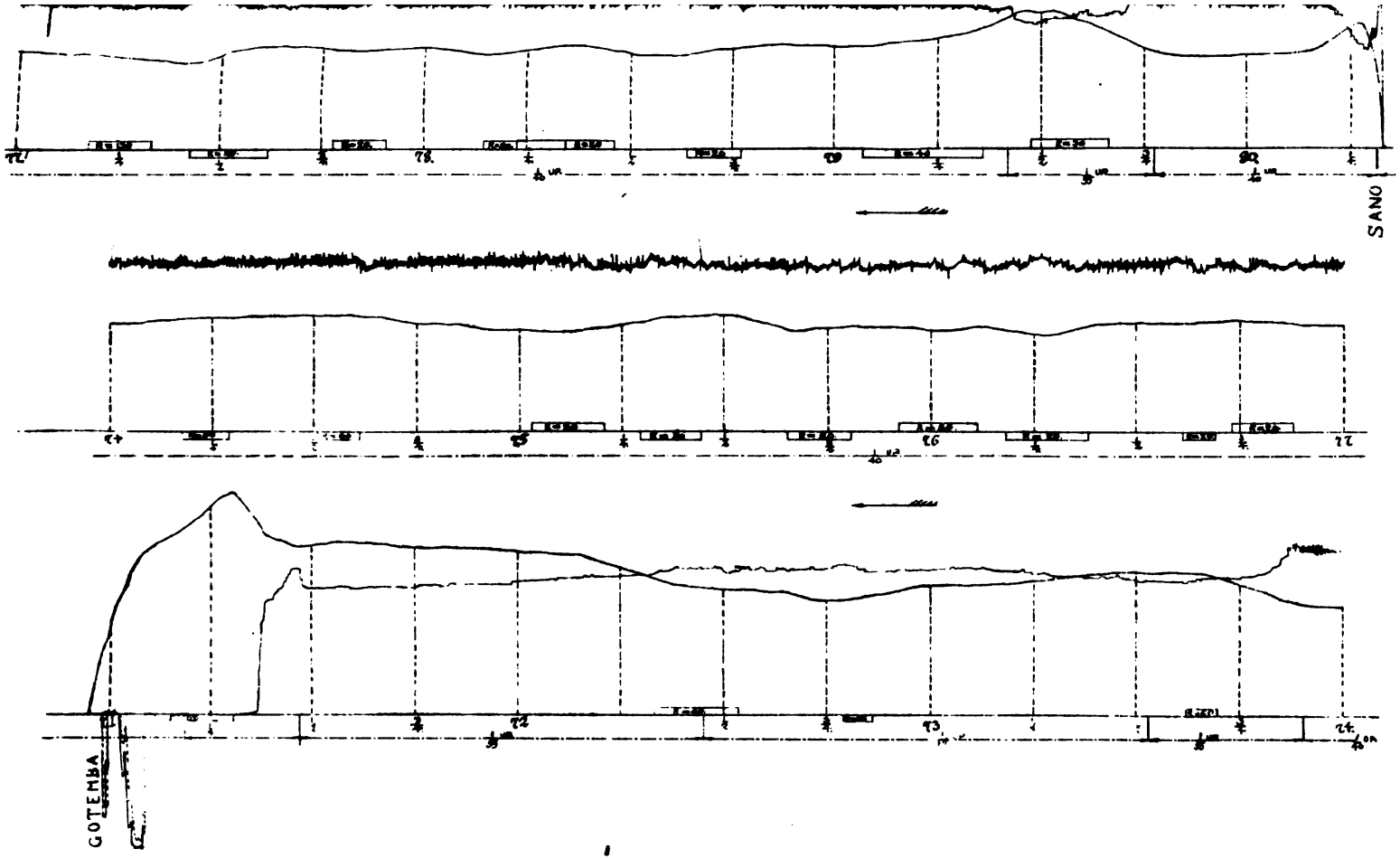
THE TRIAL RUN OF THE DYNAMOMETER CAR

JAN 22ND 1905. FROM NUMAZ TO YAMAKITA

PLATE X

FIG 42



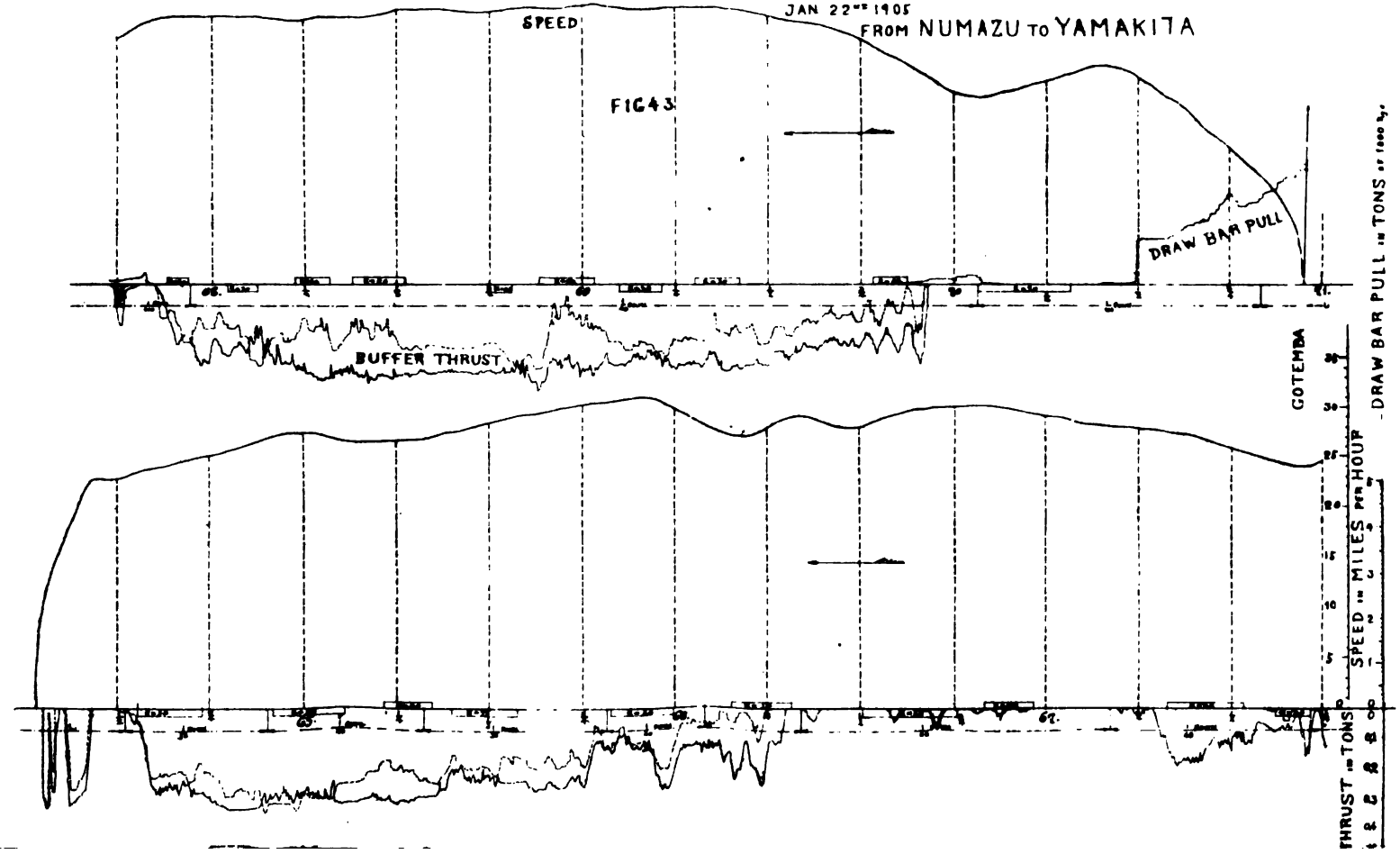

SANO
GOTEMBA

THE TRIAL RUN OF THE DYNAMOMETER CAR

PLATE XI.

JAN 22nd 1905

FROM NUMAZU TO YAMAKITA



OYAMA
YAMAKITA

THE TRIAL RUN OF THE DYNAMOMETER CAR

PLATE XII

JAN. 22. 1905

TABLE 4

	ARRIVED AT	STARTED FROM
NUMAZU		AT 9h 2m 0s A.M.
MISHIMA	AT 9h 11m 55s	16 30
SANO (Tunnel)	32 30	41 45
GOTEMBA	10 39 20	10 50 40
OYAMA	11 7 50	11 11 5
YAMAKITA	24 40	

TABLE 5
REPORT FROM NUMAZU METEOROLOGICAL OBSERVATRY

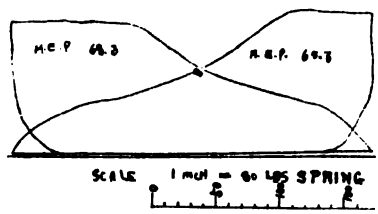
	AT 6. A.M.	AT 10 A.M.	AT 2 P.M.
BAROM.	756.0	754.6	752.4
WIND DIRECT.	E	ESE	SSE
VELOCITY m/s	6.3	4.3	1.2
TEMP. C.	7.7	8.6	11.0
TEMP. at GOTEMBA		8.1	9.1
RELATIVE % HUMIDITY	86	92	78
R.H. at GOTEMBA		98	90
PRECIPITATION	4.2 mm	2.4 mm	0.1

FROM NUMAZU TO YAMAKITA

No. 1

R

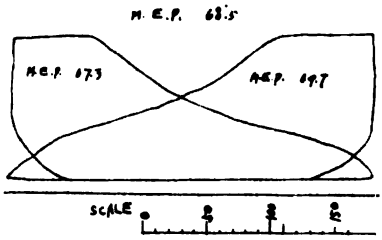
M. E. P. 66.8



REGULATOR VALVE OPENING ---------- 1¾"
BOILER PRESSURE ---------- 153 LBS
CUT OFF R F ---------- 37
R B ---------- 36.5
CUT OFF L F ---------- 34
L B ---------- 33.75
REVOLUTIONS PER MINUTE ---------- 92
SPEED OF TRAIN PER HOUR ---------- 13.4 MILES
CHIMNEY PRESSURE DIFF. BET. ATMOS. ---------- .2425
SMOKE BOX PRESSURE --- " --- " ---------- .077
EXHAUST NOZZLE PRESSURE ---------- .2071
I. H. P. R. ---------- 144.77
I. H. P. L. ---------- 133.92
I. H. P. OF ENGINE ---------- 343.23

L

M. E. P. 68.5



THE TRIAL RUN OF THE DYNAMOMETER CAR

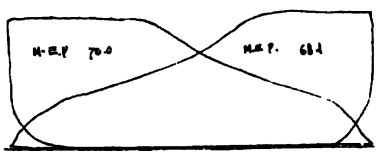
PLATE XIII

JAN 22. 1905 — ROM NUMAZU TO YAMAKITA

No 2

R

M.E.P. 69.05

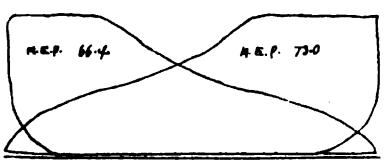


SCALE 1 INCH = 80 LBS SPRING

REGULATOR VALVE OPENING ---------- 1¼"
BOILER PRESSURE ---------- 190 LBS
CUT OFF R F ---------- 89
B ---------- 88.75
L F ---------- 87.5
B ---------- 86
REVOLUTION PER MINUTE ---------- 92
SPEED OF TRAIN PER HOUR ---------- 13.4 MILES
CHIMNEY PRESSURE DIFF BET. ATMOS. ---- .2618
SMOKE BOX PRESSURE ---------- .1083
EXHAUST NOZZLE PRESSURE ---------- .7098
I. H. P. R. ---------- 159.75
I. H. P. L ---------- 156.21
I. H. P. OF ENGINE ---------- 316.96

L

M.E.P. 69.7

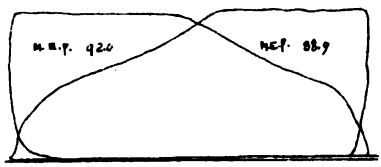


SCALE 1 INCH = 80 LBS. SPRING

No 3

R

M.E.P. 90.45

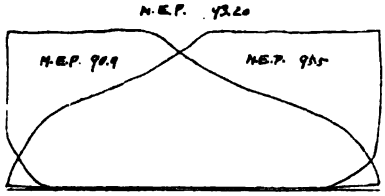


SCALE 1 INCH = 80 LBS SPRING

REGULATOR VALVE OPENING ---------- 1⅜"
BOILER PRESSURE ---------- 194 LBS
CUT OFF R F ---------- 46
B ---------- 44
L F ---------- 46.75
B ---------- 43.5
REVOLUTIONS PER MINUTE ---------- 62
SPEED OF TRAIN PER HOUR ---------- 9.03
CHIMNEY PRESSURE DIFF. BET. ATMOS. ---- .2709
SMOKE BOX PRESSURE ---------- .1088
EXHAUST NOZZLE PRESSURE ---------- .8302
I. H. P. R ---------- 136.61
I. H. P. L. ---------- 140.76
I. H. P. OF ENGINE ---------- 277.37

L

M.E.P. 93.20



SCALE 1 INCH = 80 LBS. SPRING

THE TRIAL RUN OF THE DYNAMOMETER CAR

PLATE XIV

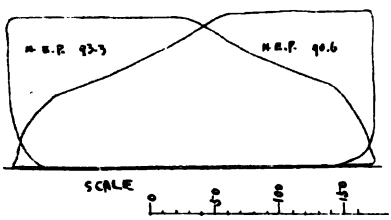
JAN. 22. 1905

FROM NUMAZU TO YAMAKITA

No. 4

R

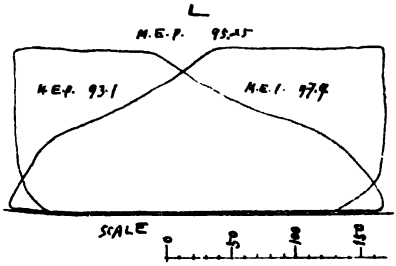
M. E. P. 91.95



REGULATOR VALVE OPENING ---------- 1 7/16"
BOILER PRESSURE ---------- 156 LBS
CUT OFF R F ---------- 46
CUT OFF R B ---------- 44
CUT OFF L F ---------- 49.75
CUT OFF L B ---------- 45.5
REVOLUTIONS PER MINUTE ---------- 62
SPEED OF TRAIN PER HOUR ---------- 9.03
CHIMNEY PRESSURE DIFF. BET. ATMOS. ---- .2985
SMOKE BOX PRESSURE ---------- .099
EXHAUST NOZZLE PRESSURE ---------- 4.571
I. H. P. R. ---------- 138.37
I. H. P. L. ---------- 143.86
I. H. P. OF ENGINE ---------- 282.73

L

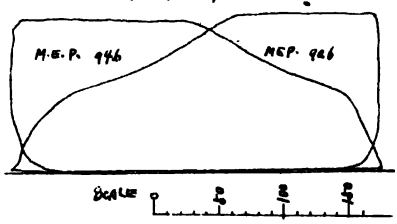
M. E. P. 95.25



No. 5

R

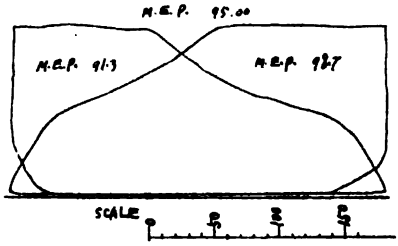
M. E. P. 95.6



REGULATOR VALVE OPENING ---------- 1 7/16"
BOILER PRESSURE ---------- 156 LBS
CUT OFF R F ---------- 46
CUT OFF R B ---------- 44
CUT OFF L F ---------- 48.75
CUT OFF L B ---------- 43.5
REVOLUTIONS PER MINUTE ---------- 62
SPEED OF TRAIN PER HOUR ---------- 9.03
CHIMNEY PRESSURE DIFF. BET. ATMOS. ---- .268
SMOKE BOX PRESSURE ---------- .113
EXHAUST NOZZLE PRESSURE ---------- 4.708
I. H. P. R. ---------- 139.36
I. H. P. L. ---------- 143.48
I. H. P. OF ENGINE ---------- 283.34

L

M. E. P. 95.00



THE TRIAL RUN OF THE DYNAMOMETER CAR

PLATE XV

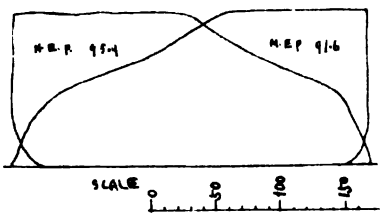
JAN. 22. 1905

FROM NUMAZU TO YAMAKITA

No 6

R.

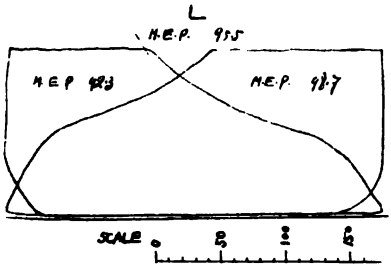
M.E.P. 93.75



REGULATOR VALVE OPENING ---------- 1 3/16"
BOILER PRESSURE ---------- 196 LBS
CUT OFF R F ---------- 96
B ---------- 89
L F ---------- 95.75
B ---------- 93.5
REVOLUTIONS PER MINUTE ---------- 58
SPEED OF TRAIN PER HOUR ---------- 2.45
CHIMNEY PRESSURE DIFF BET ATMOS. ---- .2528
SMOKE BOX PRESSURE ---- " ---------- .099
EXHAUST NOZZLE PRESSURE ---------- 2.615
I.H.P. R. ---------- 132.46
I.H.P. L ---------- 134.10
I.H.P. OF ENGINE ---------- 267.56

L

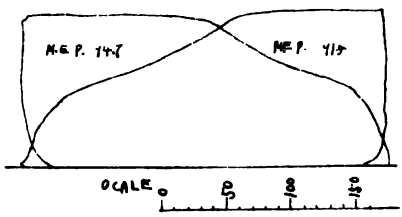
M.E.P. 95.5



No 7.

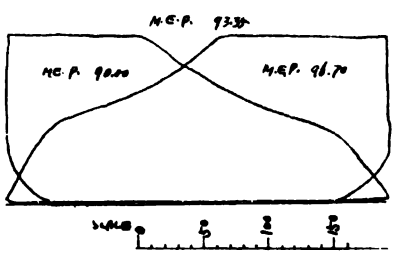
R

M.E.P. 93.1



REGULATOR VALVE OPENING ---------- 1 3/16"
BOILER PRESSORE ---------- 196 LBS
CUT OFF R F ---------- 96
B ---------- 94
L F ---------- 94.75
B ---------- 93.5
REVOLUTIONS PER MINUTE ---------- 60
SPEED OF TRAIN PER HOUR ---------- 2.79
CHIMNEY PRESSURE DIFF. BET. ATMOS. ---- .2618
SMOKE BOX PRESSURE ---------- .1013
EXHAUST NOZZLE PRESSURE ---------- 2.709
I.H.P. R. ---------- 130.07
I.H.P. L. ---------- 136.94
I.H.P. OF ENGINE ---------- 272.51

M.E.P. 93.35



THE TRIAL RUN OF THE DYNAMOMETER CAR

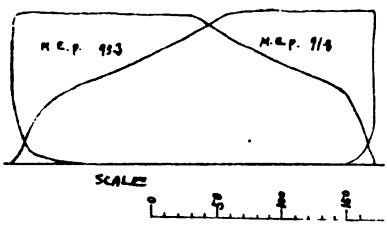
PLATE XVI

JAN. 22. 1905 — FROM NUMAZU TO YAMAKITA

No 0

R

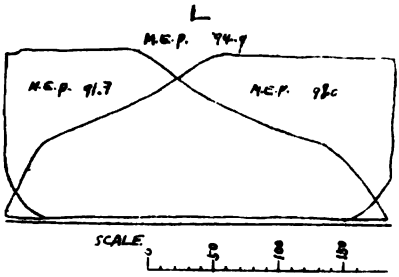
M.E.P. 93.35



REGULATOR VALVE OPENING		1 1/16"
BOILER PRESSURE		175 LBS
CUT OFF	R F	46
	R B	44
	L F	45.75
	L B	43.5
REVOLUTIONS PER MINUTE		58
SPEED OF TRAIN PER HOUR		8.45
CHIMNEY PRESSURE DIFF. BET. ATMOS.		[illegible]
SMOKE BOX PRESSURE		1.03
EXHAUST NOZZLE PRESSURE		2.70.8
I.H.P. R.		132.17
I.H.P. L.		134.08
I.H.P. OF ENGINE		266.25

L

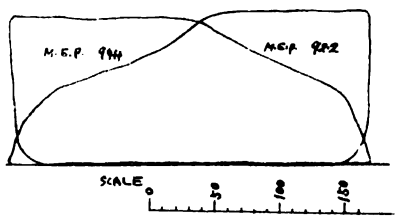
M.E.P. 94.9



No 9

R

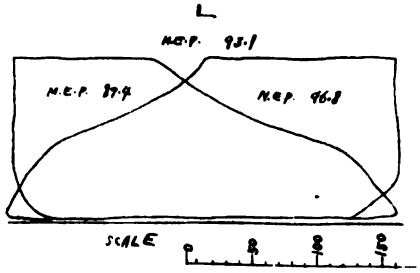
M.E.P. 93.3



REGULATOR VALVE OPENING		1 1/16"
BOILER PRESSURE		175 LBS
CUT OFF	R F	48
	R B	46.5
	L F	44.25
	L B	45
REVOLUTION PER MINUTE		66
SPEED OF TRAIN PER HOUR		9.61
CHIMNEY PRESSURE DIFF. BET. ATMOS.		[illegible]
SMOKE BOX PRESSURE		[illegible]
EXHAUST NOZZLE PRESSURE		2.9.89
I.H.P. R.		134.00
I.H.P. L.		149.68
I.H.P. OF ENGINE		277.68

L

M.E.P. 93.1



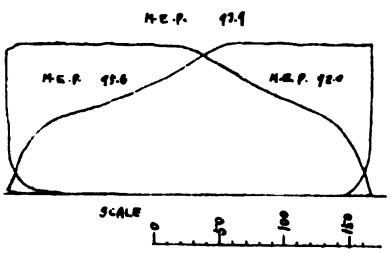
THE TRIAL RUN OF THE DYNAMOMETER CAR

PLATE XVII

JAN. 22. 1905 FROM NUMAZU TO YAMAKITA

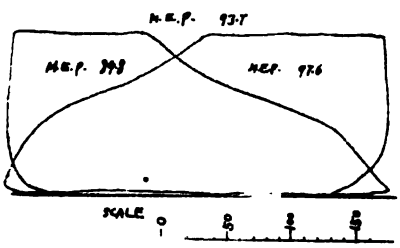
No 10

R



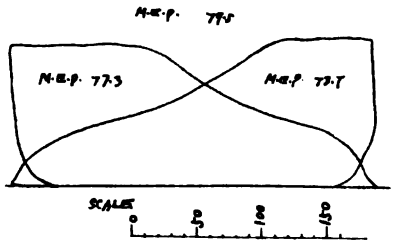
REGULATOR VALVE OPENING		1 3/8"
BOILER PRESSURE		156 LBS
CUT OFF	R F	48
	B	46.5
	L F	48.125
	B	45
REVOLUTIONS PER MINUTE		68
SPEED OF TRAIN PER HOUR		9.9
CHIMNEY PRESSURE DIFF. BET. ATMOS.		298
SMOKE BOX PRESSURE		1228
EXHAUST NOZZLE PRESSURE		3.083
I.H.P. R.		155.54
I.H.P. L.		155.21
I.H.P. OF ENGINE		310.75

L



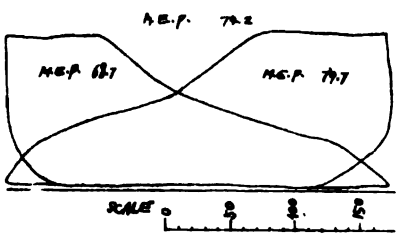
No 11

R



REGULATOR VALVE OPENING		1 3/8"
BOILER PRESSURE		156 LBS
CUT OFF	R F	35
	B	33.875
	L F	32.5
	B	30.375
REVOLUTIONS PER MINUTE		88
SPEED OF TRAIN PER HOUR		12.82
CHIMNEY PRESSURE DIFF. BET. ATMOS.		2709
SMOKE BOX PRESSURE		1173
EXHAUST NOZZLE PRESSURE		2.902
I.H.P. R.		108.45
I.H.P. L.		106.61
I.H.P. OF ENGINE		215.06

L



THE TRIAL RUN OF THE DYNAMOMETER CAR

PLATE XVII

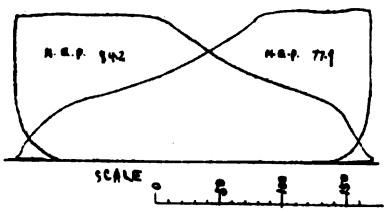
JAN. 22. 1905

FROM NUMAZU TO YAMAKITA

NO. 12

R

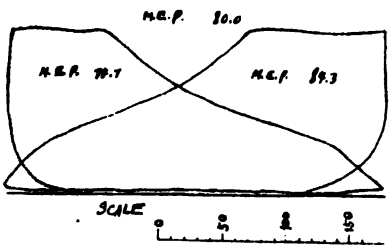
M.E.P. 91.07



REGULATOR VALVE OPENING		1 1/16"
BOILER PRESSURE		154.05
CUT OFF	R F	59
	R B	58.75
	L F	57.5
	L B	86
REVOLUTIONS PER MINUTE		70
SPEED OF TRAIN PER HOUR		41.19
CHIMNEY PRESSURE DIFF. BET ATMS.		1.017
SMOKE BOX PRESSURE		1173
EXHAUST NOZZLE PRESSURE		2.768
I. H. P. R.		173.97
I. H. P. L.		136.42
I. H. P. OF ENGINE		270.39

L

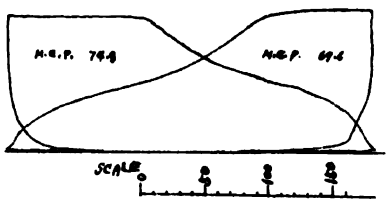
M.E.P. 80.0



NO. 13

R

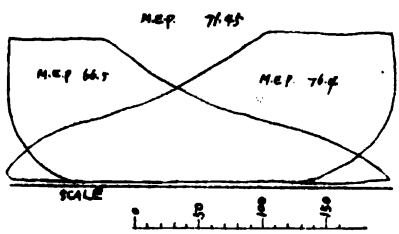
M.E.P. 72.8



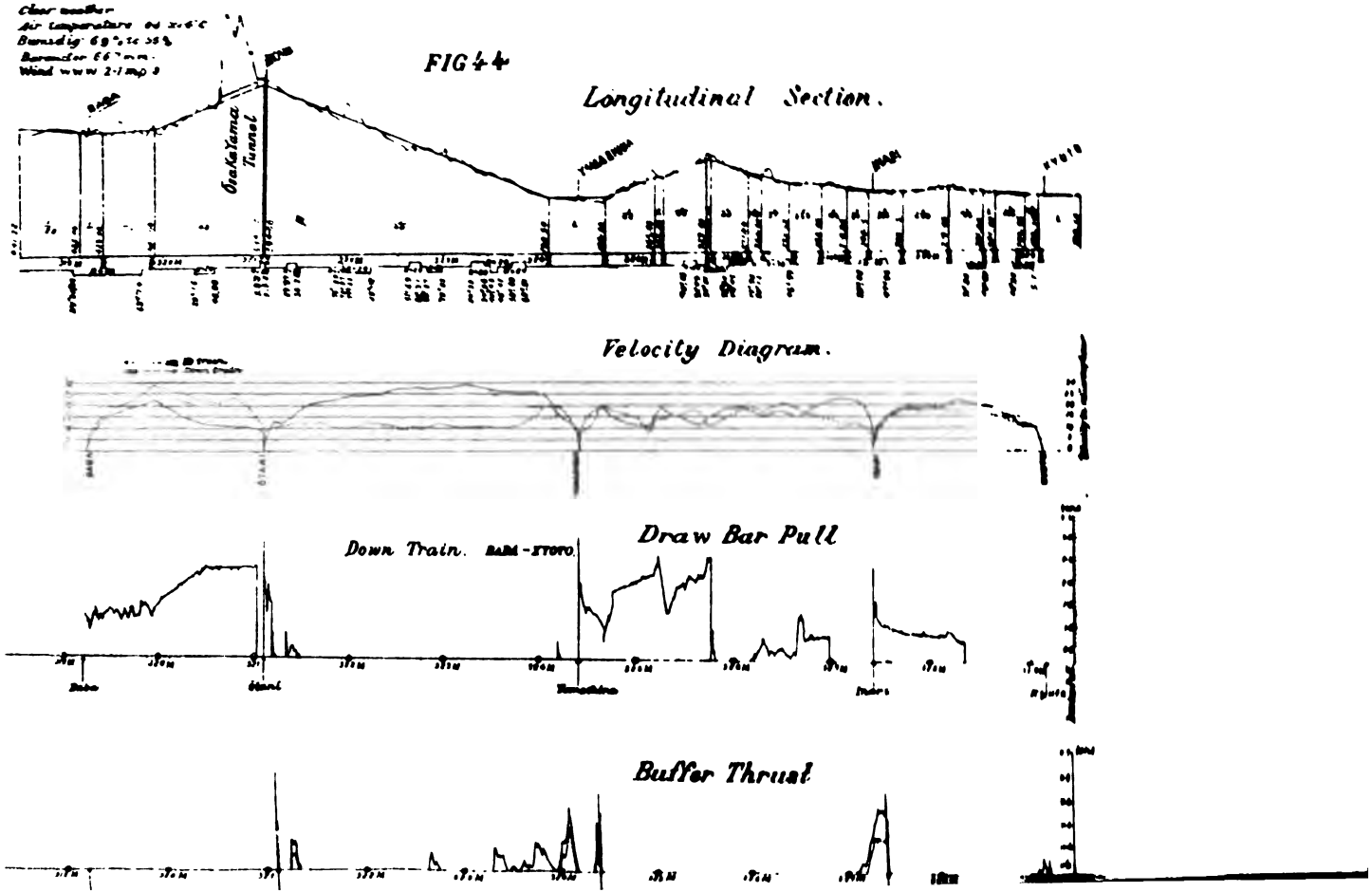
REGULATOR VALVE OPENING		1 1/16"
BOILER PRESSURE		192.05
CUT OFF	R F	59
	R B	58.75
	L F	57.5
	L B	86
REVOLUTIONS PER MINUTE		100
SPEED OF TRAIN PER HOUR		41.97
CHIMNEY PRESSURE DIFF. BET ATMS.		1.047
SMOKE BOX PRESSURE		1.045
EXHAUST NOZZLE PRESSURE		3.357
I. H. P. R.		175.88
I. H. P. L.		174.05
I. H. P. OF ENGINE		349.93

L

M.E.P. 75.45



THE TRIAL RUN OF THE DYNAMOMETER CAR. JAN 24th 1904. PLATE. XIX



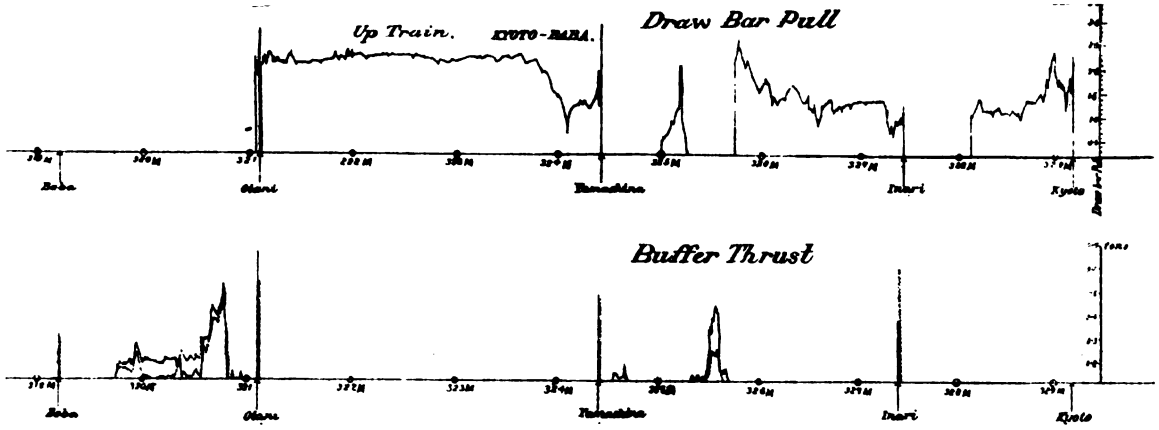
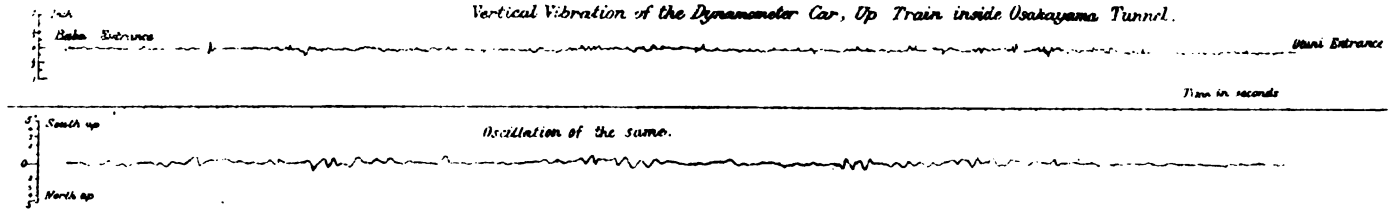
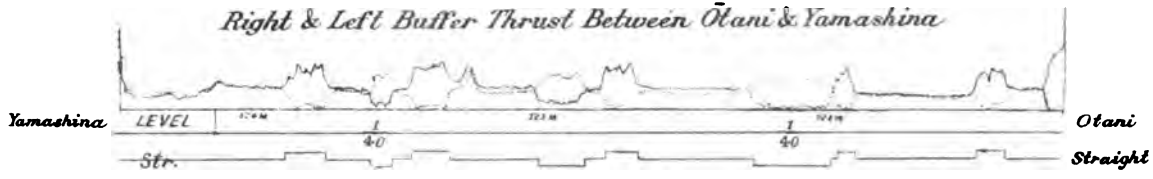

Up Train.
KYOTO-BABA.
Draw Bar Pull
Buffer Thrust
Baba
Otani
Yamashina
Inari
Kyoto

FIG 45


Vertical Vibration of the Dynamometer Car, Up Train inside Osakayama Tunnel.
Baba Entrance
Otani Entrance
Time in seconds
South up
Oscillation of the same.
North up

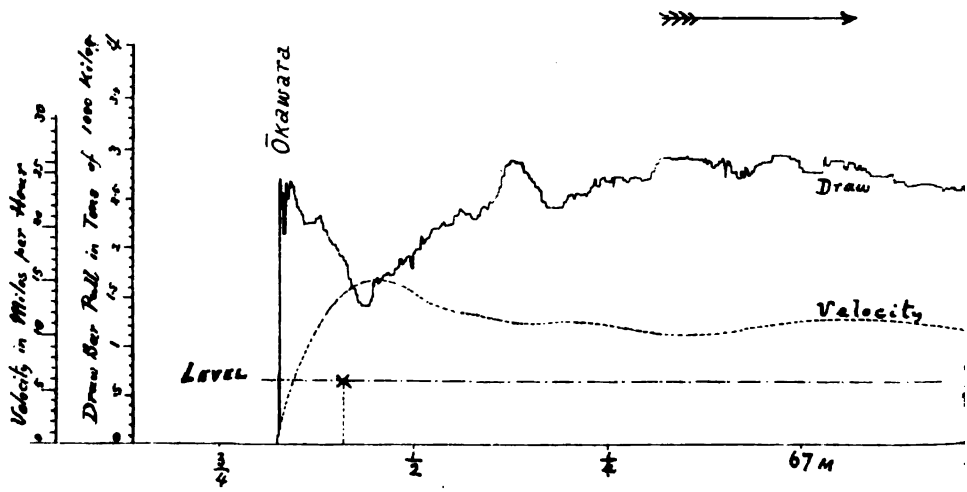

Right & Left Buffer Thrust Between Ōtani & Yamashina
Yamashina
LEVEL
1/40
1/40
Otani
Str.
Straight

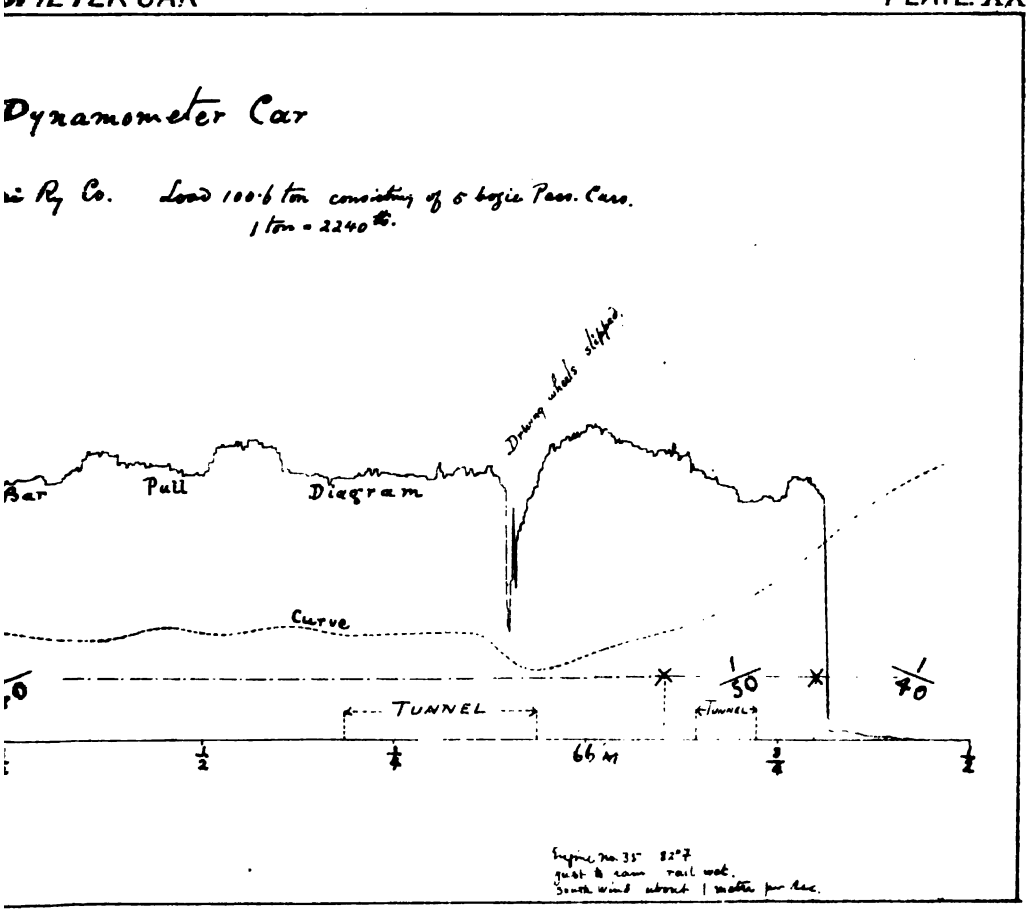
THE TRIAL RUN OF THE DYN

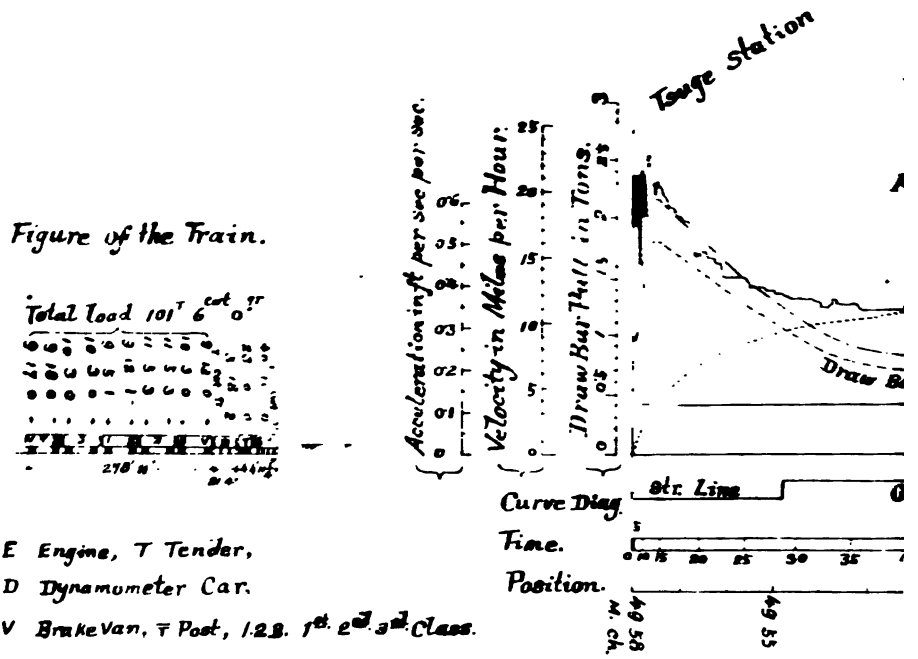
FIG. 4

Draw Bar Pull of the

July 18. 1905. Okawa Station Run

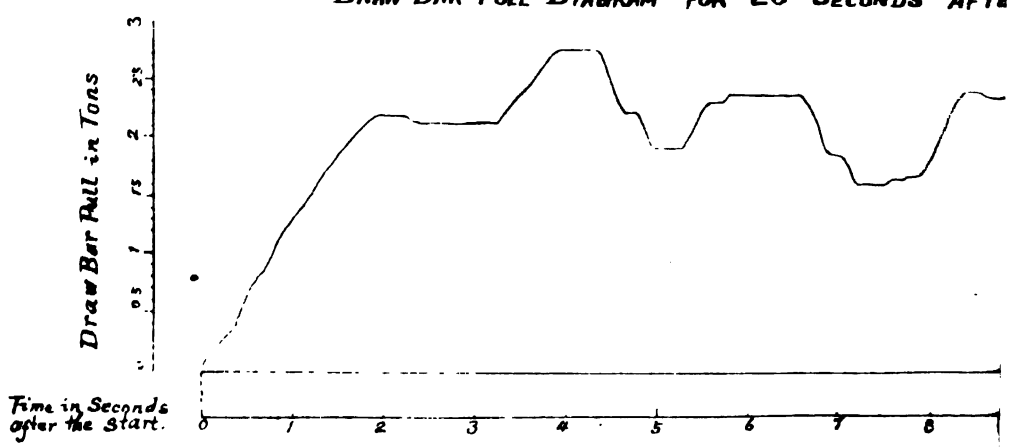



Dynamometer Car
i Ry Co. Load 100·6 ton consisting of 5 bogie Pass. Cars.
1 ton = 2240 lb.
Driving wheels slipped.
Bar
Pull
Diagram
Curve
TUNNEL
TUNNEL
1/50
1/40
1/2
1/4
66 M
3/4
1/2
Engine No. 35 82°7
gust & rain rail wet.
South wind about 1 metre per sec.



FIG

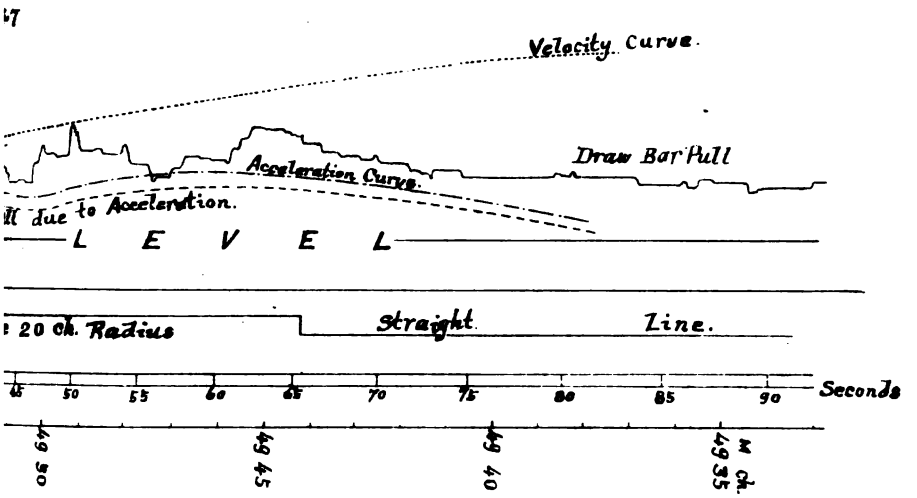
DRAW BAR PULL DIAGRAM FOR 20 SECONDS AFTE



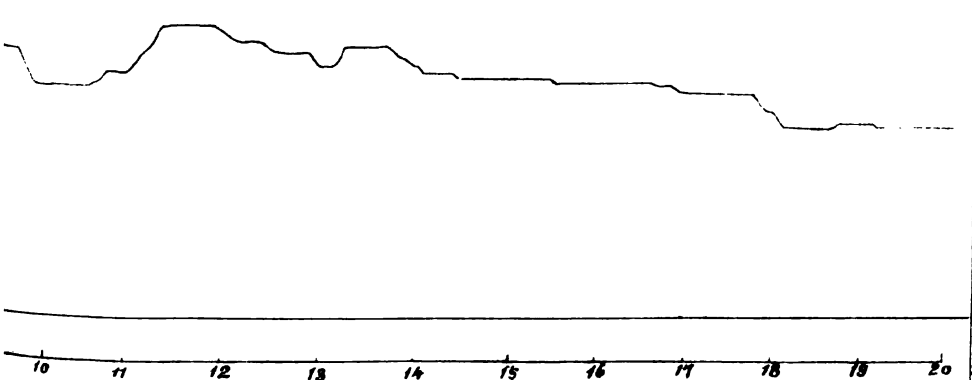
DRAW BAR PULL DIAGRAM

the Start at Tsuge Station, Kwansai Ry.

$0^h 54^m 2^s$ P.m. July 20 1905.



THE START AT TSUGE STATION. $0^h 54^m 2^s$ P.m. July 20 1905.



THE INTERIOR OF THE DYNAMOMETER CAR.

Fig. 48.

1. Recorder of the Draw Bar Pull.
2, 3. Recorders of the Buffer-thrusts.
4. Boyer's Speed Indicator.
5, 6, 7. Vibration Recorders (now not in use).

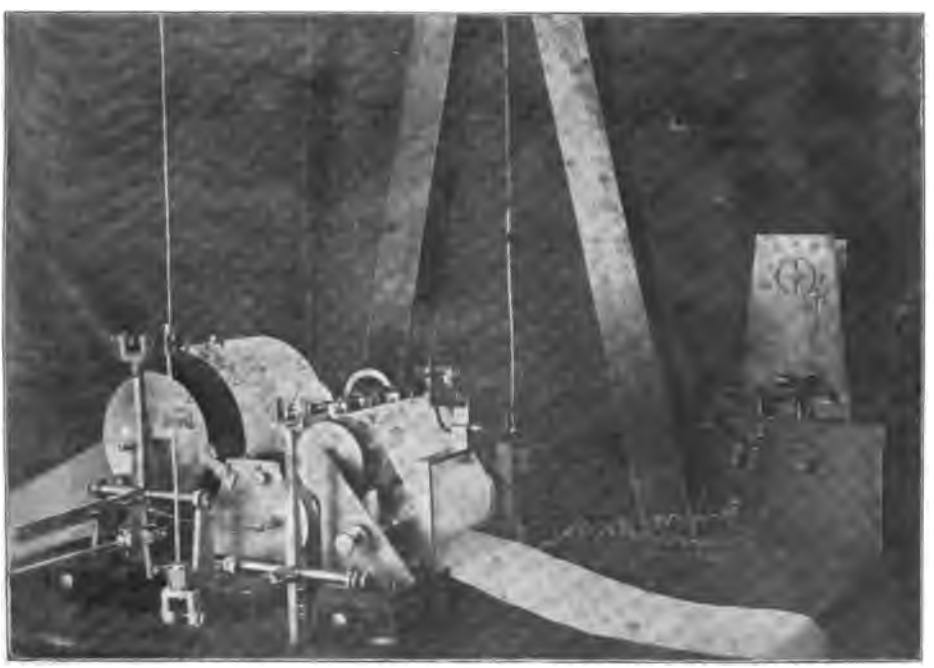


Fig. 48.

Vibration Recorder in use. In place of 5, 6 and 7.

明治四十年七月廿五日印刷
明治四十年八月一日發行

編纂兼發行者　京都帝國大學理工科大學

印刷者　東京市京橋區築地三丁目十一番地
野村宗十郎

印刷所　東京市京橋區築地二丁目十七番地
株式會社東京築地活版製造所

CONTENTS.

Equilibrium between Reciprocal Salt-Pairs.
By Yukichi Osaka and Jingoro Yamasaki. . . . 173

Reaction between Carbonic Acid and Lead Acetate in an Aqueous Solution.
By Jingoro Yamasaki. 176

Versuche zur Nutzbarmachung von Metallabfällen.
Von Toshio Watanabe. 183

Formation of Amines from the Halogen Imido Esters.
By Mitsuru Kuhara and Motooki Matsui. 187

Notes on the Refining of Copper.
By Daikichi Saito. 195

Electrolytic Dissociation of Partially Neutralised Weak Acids.
By Yûkô Mori. 205

Ueber eine einfache Methode, den Grundton eines Klanges, dessen Höhe um eine Octave unsicher ist, zu entscheiden.
Von Hanichi Muraoka. 211

Short Period Magnetographs.
By Yoshisaburô Kashiwagi. 217

On the Theory of the Rotary Converter.
By Tarô Ôtake. 228

On Beckmann's Rearrangement.
By Mitsuru Kuhara and Tadaka Kainoshô. 254

Determination of the Solubility of a Given Substance by Means of Pulfrich's Refractometer.
By Yukichi Osaka. 265

Reaction between Carbonic Acid and Lead Acetate in an Aqueous Solution. II.
By Jingoro Yamasaki. 27

Dynamometer Car Experiments. Part I.
By Sakurô Tanabe and Kakutarô Hori. . . . . 2.

MAY 8 1909
CAMBRIDGE, MASS.
Sci 125.90
(Bx an sh)
The College

MEMOIRS

OF THE

COLLEGE OF SCIENCE AND ENGINEERING,

KYŌTO IMPERIAL UNIVERSITY.

VOL. I, No. 4.

1908.

KYŌTO.

PUBLICATION COMMITTEE:

Professor	MITSURU KUHARA
Do.	MASASHI NAMBA
Do.	SAKURŌ TANABE
Do.	TOSHINOJŌ MIZUNO
Do.	YUKICHI OSAKA.

Action of Hydrogen Sulphide upon Imidoesters.

By

Motooki Matsui.

As is well known, the hydrochloride of imidoesters is so unstable towards water that it is hardly possible to keep it long without decomposition, even under a dessicator,[1] the reaction progressing in such a way as to replace the imido group with oxygen, thus:

$$\begin{array}{c} R-C-OR' \\ \| \\ NH\cdot HCl \end{array} + H_2O = \begin{array}{c} R-C-OR' \\ \| \\ O \end{array} + NH_4Cl.$$

From this fact, the question naturally arises: is it possible for the hydrogen sulphide to act similarly on the imidoester so as to yield the esters of β thio-carboxylic acids, according to the following equation?

$$\begin{array}{c} R-C-OR' \\ \| \\ NH \end{array} + H_2S = \begin{array}{c} R-C-OR' \\ \| \\ S \end{array} + NH_3 \qquad (I)$$

This reaction may be taken as analogous to the known ones which occur between the substituted amidines and hydrogen sulphide:[2] such as

$$\begin{array}{c} C_6H_5-C-NH_2 \\ \| \\ NC_6H_5 \end{array} + H_2S = \begin{array}{c} C_6H_5-C-NH_2 \\ \| \\ S \end{array} + C_6H_5NH_2$$

$$\begin{array}{c} C_6H_5-C-NHC_6H_5 \\ \| \\ NH \end{array} + H_2S = \begin{array}{c} C_6H_5-C-NHC_6H_5 \\ \| \\ S \end{array} + NH_3$$

Ber. d. chem. Ges., **16**, 355.

[2] Bernthsen: Ber. d. chem. Ges., **10**, 1240; Ann. d. chem., **192**, 33.

$$C_6H_5-\underset{\underset{NC_6H_5}{\|}}{C}-NHC_6H_5 + H_2S = C_6H_5-\underset{\underset{S}{\|}}{C}-NHC_6H_5 + C_6H_5NH_2$$

In order to settle this present question, the author conducted an experiment by passing dry hydrogen sulphide into an ethereal solution of the imidoester at ordinary temperature; by which process a substance deemed to be a sulphide of the imidoester was occasionally observed to separate, and the solution gradually became yellowish in colour, emitting a disagreeable odour. When the reaction was completed, that is, when the imidoester had wholly disappeared, the yellowish ethereal solution was treated in the manner described in the experimental part of this memoir, and was found to contain an ester of the β thiocarboxylic acid, as was expected.

It was observed, beyond what has been said, that when an ethereal solution of the imidoester into which hydrogen sulphide had been passed, is allowed to stand for a long time, the disagreeable odour, due to an ester of the thio-acid, gradually disappears and a thiamide crystallises out, on evaporation, from the ethereal solution. It seems, therefere, that the reaction expressed by the equation (I) is not final, but an intermediate one, and that the reaction progresses to form the thiamide. This second reaction, which was considered to be analogous to one that usually takes place between common esters and ammonia, was realized by the production of a thiamide from a mixture of an isolated thioester and alcoholic ammonia; being represented by the following equation:

$$R-\underset{\underset{S}{\|}}{C}-OR' + NH_3 = R-\underset{\underset{S}{\|}}{C}-NH_2 + R'OH$$

It was furthermore noticed by the author, that thioesters, such as β thio-acetic ethyl ester, -propionic ethyl ester, -benzoic ethyl ester, when treated with water, alkali or acid, replace their sulphur group by oxygen and change to ordinary esters; thus making the saponification of thioesters themselves impossible.

EXPERIMENTAL PART.

1. β THIO-ACETIC ETHYL ESTER.

$CH_3 \cdot CS \cdot OC_2H_5$.

Into an ethereal solution of imido-acetic ethyl ester, prepared by the method suggested by Pinner,[1] dry hydrogen sulphide was passed until the imidoester had completely disappeared. The yellowish solution thus obtained, after having been repeatedly washed with water to remove free hydrogen sulphide, was dehydrated over fused calcium chloride and distilled; the main portion, distilling at 105—110°, was collected and examined.

It is a yellowish mobile liquid with a very disagreeable odour, insoluble in water, but soluble in common organic solvents. It reacts very violently with concentrated nitric acid at ordinary temperature, giving acetic ethyl ester as a reaction product. A cold aqueous solution of silver nitrate easily decomposes it, yielding silver sulphide and acetic ethyl ester; lead nitrate, however, reacts very slowly when cold, but quickly when hot.

To determine the quantity of sulphur, the author put it into a small Hofmann's bulb, and the bulb, after weighing, was introduced into an Erlenmeyer flask containing a concentrated solution of silver nitrate. The flask was then closely stoppered and shaken so as to cause the liquid in the bulb to flow out. After the reaction was completed, the flask was opened and the silver sulphide was collected, well washed, dried at 100°, and then weighed. The results are stated as follows:

0·1279 gram. subtsance gave 0·3024 gram. Ag_2S

	Found	Calc. for $CH_3CSOC_2H_5$
Sulphur	30·57	30·79

To see if it does saponify, the author has treated the ester with water, caustic potash, and hydrochloric acid, conducting the experiments in a sealed tube, at a tempetature of 80°. But

[1] Ber. d. chem. Ges., 16, 1654.

sulphur in the ester being readily replaceable (changing into hydrogen sulphide or potassium sulphide), the acid corresponding to the ester could in no case be obtained by saponification.

When the ethereal solution of the imidoester, into which hydrogen sulphide has been passed, was allowed to stand for a few days and then treated as was previously mentioned, the thioester could no longer be found; but a solid substance was obtained, on evaporation of ether. The solid substance, purified by recrystallisation from hot water, was found to have all the properties of thioacetamide. The quantity of sulphur was determined by Messinger's method[1] and the result was as follows:

0·3272 gram. substance gave 1·0158 gram. $BaSO_4$

	Found	Calc. for CH_3CSNH_2
Sulphur	42·63	42·68

2. β THIO-PROPIONIC ETHYL ESTER.

$C_2H_5.CS.OC_2H_5$.

This ester was prepared from imidopropionic ethyl ester and hydrogen sulphide by a method similar to that followed in the case of β thio-acetic ethyl ester. The ester distilling at 128–130° was taken for analysis; the result being as follows:

0·1376 gram. substance gave 0·2890 gram. Ag_2S

	Found	Calc. for $C_2H_5CSOC_2H_5$
Sulphur	27·16	27·14

It is a yellow liquid having a very disagreeable odour, and its chemical behaviour is similar to that of the thio-acetic ester; except that it does not form thiopropiamide interacting with alcoholic ammonia.

3. β THIO-BENZOIC ETHYL ESTER.

$C_6H_5.CS.OC_2H_5$.

To prepare this, the author passed dry hydrogen sulphide into

[1] Ber. d. chem. Ges., 21, 2914.

an ethereal solution of imidobenzoic ethyl ester, whereupon the solution became yellowish and at the same time some brown, oily liquid separated out; this last, upon standing, solidified in crystallising into radiated needles.

It is a yellow liquid of a very disagreeable odour, having the chemical behaviour analogous to that of the two thioesters above described. It changes into thiobenzamide when kept long in contact with alcoholic ammonia. When ether was evaporated from the ethereal solution of imidobenzoic ethyl ester saturated with hydrogen sulphide and kept for a long time, an amorphous, pale yellow mass, having the appearance of butter, was found to remain as a residue. It was well pressed between filter papers to free it from thioester, and purified by recrystalisation from hot water or chloroform. Upon analysing it and examining its properties, the substance was confirmed as being thiobenzamide.

0·1360 gram. substance gave 0·2317 gram. $BaSO_4$

	Found	Calc. for $C_6H_5CSNH_2$
Sulphur	23·4	23·4

Determination of the Solubility of a Given Substance by Means of Pulfrich's Refractometer.

(*Second Communication.*)

By

Yukichi Osaka.

While the solubility of inorganic compounds has hitherto been studied extensively, in most cases with tolerable accuracy, the results have not been so fruitful in the case of organic compounds. The reason for this latter fact may probably be found in the experimental difficulties, on account of the volatile and indifferent nature of the materials. In a preliminary communication,[1] it was already shown by the author that the solubility of a substance which is volatile and difficult to estimate chemically in its solutions, and to which, consequently, the common methods of solubility determination cannot be applied, may easily be determined by means of Pulfrich's refractometer. Since then the method has been tested more extensively with different substances for the purpose of determining its advantage and reliability, and the results thus far obtained are shown in the present communication.

Let δ be the angle directly observed in the refractometer with a solvent in the cylinder, and δ' the angle observed similarly with a solution, 100 grams of which contained x grams of a solute. Now, as shown in the previous article, we have the following empirical relation:

$$ax + bx^2 = \delta - \delta' = \Delta,$$

[1] These Memoirs, 1, 265.

where a and b are constants depending on the nature of the solvent and the solute, and Δ is the difference of the observed angles. It was also shown previously, that we have a similar formula when x denotes the amount of a solute in 100 c. c. of a solution; but as the solubility of a substance is usually expressed as its amount contained in 100 grams of a solvent, this method of calculation was not further investigated.

The constants a and b may be determined by the experiments with the solutions of two known concentrations. In order to ascertain the exactness of the formula and the limits of the concentrations within which one and the same formula may be applied, the solutions of more than two different known concentrations were subjected to refractometric observation and from the data thus obtained a and b were calculated by the method of the least square.

1. Mercuric Chloride in Water.

Recrystallised mercuric chloride, and water free from carbonic acid were used.

Table 1.

Solute in grams.	Solution in grams.	δ'	Δ	x	
				Exp.	Calc.
0	—	67° 32′	0	—	—
0·411	15·265	67° 21′	0·50°	2·69	2·70
0·584	15·542	66° 50′	0·70°	3·76	3·75
0·812	15·774	66° 33′	0·98°	5·15	5·18
0·971	15·934	66° 22′	1·16°	6·09	6·09
Saturated.		66° 6′	1·43°	—	6·82

From these experimental data we have:

$$0{\cdot}1817x + 0{\cdot}00149x^2 = \Delta$$

or

$$x = \sqrt{\frac{5{\cdot}52 + \Delta}{0{\cdot}00149}} - 60{\cdot}76$$

In table 1., the values of x calculated by the formula, are given in the last column, and, as is seen, the agreement between the experimental and the calculated values is quite satisfactory.

From the calculated value of x for the saturated solution, the solubility, or the amount of the solute in 100 grams of the solvent, is calculated to be 7·42, which very closely agrees with the value, 7·4, as found by H. W. Foote.[1]

2. Sodium Chlorate in Water.

Sodium chlorate (*puriss*) from Schuchardt in Goerlitz was used.

Table 2.

Solute in grams.	Solution in grams.	δ'	Δ	x	
				Exp.	Calc.
0	—	67° 32′	0	—	—
1·281	6·199	63° 25′	4·12°	20·67	20·5
1·968	6·942	61° 42′	5·83°	28·34	28·6
2·619	7·592	60° 23′	7·08°	34·49	34·3
3·274	8·114	59° 6′	8·43°	40·34	40·3
Saturated		56° 49′	10·72°	—	50·3

From these experimental data we have:

$$0{\cdot}192x + 0{\cdot}000414x^2 = \Delta$$

or

$$x = \sqrt{\frac{22{\cdot}27 + \Delta}{0{\cdot}000414}} - 232{\cdot}0.$$

[1] Amer. Chem. Journ., **30**, 339 (1903).

As seen in the table, the agreement between the experimental and calculated values of x is satisfactory. The solubility is found by calculation to be 101. As to the solubility of sodium chlorate in water, we notice in the literature the following values:[1]

Temperature:	12°	15°	20°	40°	60°	80°	100°
Solubility:	82	89½	91	123½	147	175	204
Observer:	Kremer		Graebe	Kremer			

On describing a solubility curve from Kremer's data, we shall find that the solubility at 20° and 25°, as estimated on the curve, is higher than those given by Graebe and the author respectively.

3. Cane Sugar in Water.

Cane sugar, precipitated from a cold saturated solution of sugar candy with absolute alcohol, washed with freshly rectified ether and dried, was used.

Table 3.

Solute in grams.	Solution in grams.	ϑ'	Δ	x	
				Exp.	Calc.
0	—	67° 32′	0	—	—
1·013	6·000	62° 22′	5·17°	16·88	17·3
2·988	7·999	55° 55′	11·62°	37·35	37·3
2·991	6·022	51° 50′	15·70°	49·67	49·3
4·230	7·220	48° 35′	18·95°	58·59	58·4
5·361	8·405	46° 37′	20·92°	63·79	63·9
Saturated		45° 8′	22·40°	—	68·0

[1] Landolt, Bernstein, Meyerhoffer's Tabellen, S. 557.

From these experimental data, we have:

$$0{\cdot}2898x + 0{\cdot}000585x^2 = \Delta$$

or

$$x = \sqrt{\frac{35{\cdot}90 + \Delta}{0{\cdot}000585}} - 247{\cdot}7$$

As seen from the table, the concordance between the experimental and calculated values of x, is satisfactory, with the exception of one case only, in which the concentration is comparatively low. Hence, it is not advisable to apply the formula to too wide a range of concentrations; and, indeed, it is not necessary, in the solubility determination, to take solutions of such wide difference in concentration. The solubility of cane sugar is found from the data to be 212, which is in accord with 211·4, as determined by Herzfeld.[1]

4. Disodium Hydrogen Phosphate in Water.

Disodium hydrogen phosphate was thrice recrystallised, and its water of crystallisation ascertained by analysis to correspond to the formula $PO_4HNa_2{\cdot}12H_2O$.

Table 4.

Solute in grams.	Solution in grams.	δ'	Δ	x	
				Exp.	Calc.
0	—	67° 32′	0	—	—
0·999	15·932	66° 33′	0·98°	2·49	2·48
2·480	17·402	65° 20·5′	2·20°	5·65	5·66
3·972	18·905	64° 20′	3·20°	8·33	8·33
5·449	20·356	63° 31′	4·02°	10·61	10·59
Saturated		63° 28′	4·07°	—	10·73

[1] Landolt, Bernstein, Meyerhoffer's Tabellen, S. 584.

Here x denotes the amount of the salt as anhydrous. From these data we have:

$$0{\cdot}400x - 0{\cdot}00193x^2 = \Delta$$

or

$$x = 103{\cdot}75 - \sqrt{\frac{20{\cdot}75 - \Delta}{0{\cdot}00193}}$$

The agreement between the experimental and calculated values of x is quite satisfactory, and the solubility of the salt is found to be 12·2. The results of the solubility determinations of this salt, as found in literature,[1] are widely discordant; as may be seen from the following citations:

	Temperature:	20°	25°	30°
Solubility	(Mulder)	9·3	15·4	24·1
	(Poggiale)	11·08	—	19·95
	(Neese)	6·8	12·5	

The present author's result, it will be noted, is not greatly divergent from that of Neese. Experiments on the solubility determination of this salt, at different temperatures by a common method, are now in progress in the author's laboratory and the result so far reached at 25° is in good accord with the author's determination.

5. Borax in Water.

Recrystallised borax was analysed for its water of crystallisation, by which analysis it was confirmed as corresponding to the formula $B_4O_7Na_2 . 10H_2O$.

[1] Cf. Comey's Dictionary of Chemical Solubility, p. 310.

Table 5.

Solute in grams.	Solution in grams.	δ'	Δ	x	
				Exp.	Calc.
0	—	67° 31′	0	—	—
0·409	15·904	66° 54·5′	0·63°	1·36	1·39
0·605	15·736	66° 40′	0·87°	2·03	2·01
0·797	15·531	66° 26′	1·10°	2·71	2·68
Saturated		66° 16′	1·27°	—	3·23
0·963	15·356	66° 14′	1·30°	3·32	3·34

Here, x refers to the anhydrous salt, and the last solution given in the table was a supersaturated one. From these experimental data, we obtain:

$$0{\cdot}498x - 0{\cdot}0326x^2 = \Delta$$

or

$$x = 7{\cdot}63 - \sqrt{\frac{1{\cdot}90 - \Delta}{0{\cdot}0326}}$$

As is seen, the agreement between the experimental and calculated values of x is quite satisfactory. The solubility is found to be 3·33, which does not vary much from the value, 3·23, found graphically from data given by D. W. Horn and E. M. van Wagener,[1] but it is quite divergent from the value, 4.98, similarly obtained from the Poggiale's data given in Comey's Dictionary of Chemical Solubility.[2]

6. Mercuric Chloride in Alcohol.

Ethyl alcohol of 99·2 per cent. by weight was used.

[1] Amer. Chem. Journ., **30**, 347 (1903).

[2] p. 55.

Table 6.

Solute in grams.	Solution in grams.	δ'	Δ	x	
				Exp.	Calc.
0	—	62° 5′	0	—	—
0·434	4·372	60° 40′	1·41°	9·94	9·63
0·805	4·715	59° 31′	2·67°	17·01	17·29
1·188	5·175	58° 24′	3·68°	22·95	22·89
1·490	5·460	57° 35′	4·50°	27·28	27·19
Saturated		56° 20′	5·75°	—	33·38

From these experimental data, we obtain:

$$0{\cdot}135x + 0{\cdot}00110x^2 = \Delta$$

or

$$x = \sqrt{\frac{4{\cdot}14\Delta}{0{\cdot}00110}} - 61{\cdot}26$$

The experimental and calculated values of x agree pretty well, excepting those cases in which the concentrations are comparatively low.

7. Cumarin in Chloroform.

Cumarin and chloroform (from chloral) from Schuchardt in Goerlitz were used.

Table 7.

Solute in grams.	Solution in grams.	δ'	Δ	x	
				Exp.	Calc.
0	—	47° 59′	0	—	—
0·494	3·413	42° 6·5′	5·88°	14·46	14·6
0·733	3·712	40° 11′	7·80°	19·75	19·6
0·992	3·962	38° 8·5′	9·84°	25·05	25·0
0·951	3·160	36° 18′	11·68°	30·11	30·1
0·302	3·541	33° 57′	14·03°	36·76	36·7
Saturated		29° 42·5′	18·28°	—	49·4

From these data we obtain:

$$0{\cdot}416x - 0{\cdot}00093x^2 = \Delta$$

or

$$x = 22{\cdot}30 - \sqrt{\frac{46{\cdot}41 - \Delta}{0{\cdot}00093}}$$

The agreement between the experimental and calculated values of x is found to be satisfactory.

8. Benzophenone in Benzene.

Benzophene from Schuchardt in Goerlitz, and benzene (free from thiophene) from Merck in Darmstadt were used.

Table 8.

Solute in grams.	Solution in grams.	δ'	Δ	x	
				Exp.	Calc.
0	—	64° 11′	0	—	—
0·494	1·432	57° 14′	6·95°	34·50	34·7
0 985	1·918	53° 55′	10·27°	51·36	51·4
1·477	2·351	51° 40′	12·52°	62·82	62·6
1·970	2·883	50° 31′	13·67°	68·33	68·3
Saturated		48° 28′	15·72°	—	78·6

From these data we obtain:

$$x = \frac{\Delta}{0{\cdot}200},$$

and the experimental and calculated values of x agree with each other satisfactorily.

9. Mercuric Chloride in a Normal Aqueous Solution of Sodium Chloride.

A normal solution of sodium chloride was used as the solvent.

Table 9.

Solute in grams.	Solution in grams.	δ'	Δ	x	
				Exp.	Calc.
0	—	65° 28′	0	—	—
0·881	16·432	64° 26′	1·03°	5·36	5·34
1·993	17·532	63° 12′	2·27°	11·37	11·39
3·505	19·043	61° 39·5′	3·81°	18·40	18·40
4·845	20·388	50° 24′	5·07°	23·77	23·79
Saturated		50° 5′	5·38°	—	25·08

From these data we have:

$$0{\cdot}1864x + 0{\cdot}00112x^2 = \Delta$$

or

$$x = \sqrt{\frac{7{\cdot}76 + \Delta}{0{\cdot}0012}} - 83.28$$

The experimental and calculated values of x show perfect agreement. It is a well known fact that sodium and mercuric chlorides will form complex salts in solutions, as may be seen, among others, by the increased solubility of mercuric chloride in the sodium chloride solutions as in pure water. Thus, it is now experimentally proved that the author's formula may be applied equally well even when chemical reactions takes place between the solvent and solute.

As has been repeatedly remarked, for the solubility determination of a substance at a given temperature, two solutions of known concentration are necessary and quite sufficient. When, however,

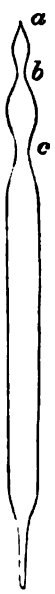
we determine the limit of concentrations between which a given formula may be applied by using more than two solutions, it is possible to use the same formula for the solubility determinations of the same substance at other temperatures. For example: If we have to determine the solubility of a given substance in a given solvent, at a temperature higher than that at which the author's formula for such solute and solvent has already been calculated; and if the solubility in question increases with temperature, we have to proceed as follows: A known quantity of the saturated solution at the given higher temperature is diluted with a known quantity of the solvent,—the quantities of the two being in such ratio that, on lowering the temperature to that degree at which we have the formula for calculation, no separation of the solute will take place;—thus the concentration of the diluted solution falls within the limits of the applicability of the formula.

The refractometric method of the solubility determinations can be worked with small quantities of materials: as is verified by the two series of experiments conducted as follows:

10. Sodium Chloride in Water.

A glass tube, about 15 cm. long and 0·7 wide, was drawn out at one end and closed by fusion. The tube was weighed; a small quantity of sodium chloride introduced and the tube weighed again; a small quantity of water was added, the other end of the tube closed by fusion, and the whole weighed again. By shaking violently the dissolution was completed. Then, the wider end of the tube was filed off, the open end was put into the cylinder of the refractometer, into which the solution was made to flow when the narrow end of the tube had been broken, and then the observations were made as usual. In the experiments, two such tubes were required for the determination of the constants of the formula.

The study of the saturated solution was conducted in the following way, namely: 1 gram of sodium chloride and 1·5 grams of water, each approximately weighed, were introduced into a glass tube prepared as above described. Near its wider end, the tube was drawn out twice, at *b* and *c*, as shown in the annexed figure, and then closed by fusion at *a*. The tube was now shaken, and put into a thermostat at 25°, for a certain period of time sufficient for saturation of the solution. The tube was then opened at *b*, some purified cotton introduced between *b* and *c*, and the open end brought into the cylinder of the refractometer. The other end of the tube was then broken by pinching between the fingers and the clear solution, filtered through the cotton, was made to run into the refractometer by blowing at the other end.



The result was as follows:

Table 10.

Solute in grams.	Solvent in grams.	Solution in grams.	δ'	Δ	x
0	—	—	67° 32′	0	—
0·1943	1·0250	1·2143	61° 59′	5·55°	15·93
0·2984	1·0162	1·3146	59° 44′	7·80°	22·70
Saturated solution			58° 30′	9·03°	—

From these experimental data we have:

$$0{\cdot}359x - 0{\cdot}00069x^2 = \Delta$$

or

$$x = 260{\cdot}0\sqrt{\frac{46{\cdot}70 - \Delta}{0{\cdot}00069}}$$

This formula gives $x = 26{\cdot}5$ for the saturated solution, and the

solubility of sodium chloride in water at 25° is found to be 36·0. Now, the correctness of the value found will be seen by comparison with the following figures stated in the literature:[1]

Kopp.	Müller.	Andreae.	Raupenstrauch.	Poggiale.	Mulder.
35·7	35·81	35·93	35·96	36·13	36·1

11. Potassium Sulphate in Water.

The experimental method was the same as the last.

Table 11.

Solute in grams.	Solvent in grams.	Solution in grams.	δ'	Δ	x
0	—	—	67° 32′	0	—
0·0669	0·9095	0·9764	65° 48′	1·73°	6·87
0·0967	0·9648	1·0615	65° 16′	2·27°	9·01
Saturated solution			64° 49′	2·70°	—

These experimental data give:

$$x=\sqrt{\frac{\Delta}{0{\cdot}252}}$$

The value of x for the saturated solution is found to be 10·72 by calculation and the solubility 12·0. This value is concordant with the following numbers given in the literature:[2]

Trevor.	Meyerhoffer.
12·04	12·06

Summary.

1. The determination of the solubility of a substance which

[1] Cf. Landolt, Bernstein, Meyerhoffer's Tabellen, S. 556; and Comey's Dictionary of Chemical Solubility, p. 376.

[2] Landolt, Bernstein, Meyerhoffer's Tabellen, S. 547.

cannot be done by the common methods, may easily be conducted by means of Pulfrich's refractometer, when the solubility is not too small.

2. The results obtained by the author's method are equally reliable with those by the common methods.

3. The formula:

$$ax + bx^2 = J$$

is available within a tolerably wide range of concentrations.

4. The constants in the formula are different at different temperatures; but one and the same formula, determined for a particular temperature, may be used in the solubility determinations at other temperatures with some modifications of the experimental method.

5. The formula may be applied to cases in which a solution is used as a solvent.

6. The formula is equally applicable to those cases in which chemical reaction takes place between a solvent and a solute.

7. The author's method for the solubility determination may be carried out accurately with small quantities of solvents and solutes.

January, 1908.

On the Birotation of d-Glucose. II.

By

Yukichi Osaka.

In one[1] of the author's previous articles, it has been shown, among other things, that the velocity of the retrogression of the rotatory power of d-glucose is approximately proportional to the concentration of the hydroxyl ions, and also to the square root of that of the hydrogen ions. The present article deals with the influence of temperature on the reaction, and also with the catalytic action of a weak acid and of its neutral salt in presence of a free acid, as the author called in question the conclusions upon the same subject which Trey had drawn from his experiments.

d-Glucose was purified by the method given by Soxhlet, as conducted in the previous experiments, and the water used was that redistilled with a tin-condenser and freed from carbonic acid.

1 gram of the anhydrous d-glucose was dissolved in a small quantity of water, a catalyser was added, if necessary, and the solution was then diluted to 20 c. c. The solution thus prepared was subjected to polarimetric observation in a tube 2 dcm. long, by means of a polarimeter after Landolt with a Lippich's polariser, water of a thermostat being kept circulating through the mantel of the observation tube. The temperature during the experiments was kept at 20°, except in some special cases.

The velocity constant of the reaction was calculated by the following formula:

$$k=\frac{1}{t}\log\frac{a_0-a_x}{a-a_x},$$

where a_0 denotes the rotation of the solution at the time when

[1] Zeitschr. f. physik. Chem., **35**, 661 (1900).

the observation was begun, a_∞ that at the end of the reaction, and a that at the time t.

1. Influence of Temperature.

Levy[1] has shown that the concentration of d-glucose between 0·9 and 5·0 per cent. has no influence on the velocity of the retrogression of its rotatory power, and that the velocity is increased by about 5 per cent. when the temperature is raised by 0·15°, as calculated from data at the temperatures, 20·25° and 20·1°, which do not differ much from each other. It was, therefore, desirable to investigate the influence of temperature on the reaction in some wider intervals of temperature. The experimental results were as follows:

Table 1.

Temperature 15°.

t	$a-a_\infty$			$k.\ 10^3$		
(min.)	(1)	(2)	(3)	(1)	(2)	(3)
0	4·57°	4·68°	4·89	—	—	—
10	4·18	4·29	4·48	3·9	3·8	3·8
20	3·82	3·94	4·08	3·9	3·7	3·9
30	3·52	3·58	3·74	3·8	3·9	3·9
40	3·21	3·32	3·42	3·8	3·7	3·9
50	2·95	3·01	3·13	3·8	3·8	3·9
60	2·70	2·76	2·90	3·8	3·8	3·8
70	2·45	2·52	2·66	3·9	3·8	3·8
				3·8	3·8	3·9

Mean: $3{\cdot}8.10^{-3}$

[1] Zeitschr. f. physik. Chem. **17**, 301 (1895).

Table 2.

Temperature 20°.

t	$a-a_\infty$			$k.\ 10^3$		
(min.)	(1)	(2)	(3)	(1)	(2)	(3)
0	4·35°	4·63°	4·12°	—	—	—
5	4·03	4·30	3·82	6·6	6·4	6·6
12	3·63	3·85	3·41	6·6	6·7	6·8
20	3·21	3·42	3·02	6·6	6·6	6·7
30	2·78	2·94	2·63	6·5	6·6	6·5
45	2·21	2·35	2·09	6·5	6·5	6·6
65	1·64	1·72	1·54	6·5	6·6	6·6
				6·6	6·6	6·6

Mean : $6{\cdot}6.10^{-3}$

Table 3.

Temperature 25°.

t	$a-a_\infty$			$k.\ 10^3$		
(min.)	(1)	(2)	(3)	(1)	(2)	(3)
0	4·29°	4·04°	3·25°	—	—	—
5	3·72	3·58	2·88	10·3	10·5	10·4
12	3·06	3·04	2·44	10·2	10·2	10·3
20	2·42	2·47	1·99	10·2	10·7	10·6
30	1·85	1·93	1·59	10·2	10·7	10·4
45	1·24	1·31	1·08	10·2	10·8	10·6
65	0·71	0·78	0·69	10·2	11·0	10·4
				10·2	10·6	10·4

Mean : $10{\cdot}4.10^{-3}$

As seen from the tables, the ratio of the velocities at 25° and 15° is 2·7, and the influence of temperature on the reaction in question is of the same order as in most other cases.

Using the first and last data for the calculation of the well-known formula of Arrhenius, which represents the relation between temperature and reaction velocity, we obtain:

$$\log k.10^3 = -\frac{3753}{t} + 13{\cdot}61$$

and it gives for 20°

$$k = 6{\cdot}3.10^{-3}$$

while the experimental value is found to be $6{\cdot}6.10^{-3}$.

2. Catalytic Action of a Neutral Salt.

By experimenting with 5 and 10 per cent. solutions of sodium chloride, Levy[1] showed that the presence of sodium chloride decreases the velocity of the retrogression of the rotatory power of d-glucose, and this view has been confirmed by Trey[2] with the solution of a dilution of 10 litres. The author has now undertaken the study with the same neutral salt, as it was not without interest to compare its action when by itself with that in the presence of free acid. In the following tables v denotes the dilution of the solution in litres; that is, the number of litres in which a mol of the salt is contained.

Table 4.

Sodium chloride $v = 15$.

t	$a - a_\infty$		$k.\ 10^3$	
(min.)	(1)	(2)	(1)	(2)
0	4·37°	4·07°	—	—
5	4·04	3·75	6·8	7·1
12	3·65	3·40	6·5	6·5
20	3·22	3·01	6·6	6·6
30	2·77	2·60	6·6	6·5

[1] Loc. cit.

[2] Zeitschr. f. physik. Chem., **22**, 424 (1897).

t	$a-a_\infty$		$k.\ 10^3$	
(min.)	(1)	(2)	(1)	(2)
45	2·20	2·04	6·6	6·7
65	1·62	1·52	6·6	6·6
			6·6	6·7

Table 5.

Sodium chloride $v=10$.

t	$a-a_\infty$		$k.\ 10^3$	
(min.)	(1)	(2)	(1)	(2)
0	4·47°	4·59°	—	—
5	4·16	4·26	6·2	6·5
12	3·75	3·86	6·4	6·3
20	3·34	3·43	6·3	6·3
30	2·88	2·98	6·4	6·3
45	2·35	2·37	6·2	6·4
65	1·73	1·78	6·3	6·3
			6·3	6·3

Table 6.

Sodium chloride $v=5$.

t	$a-a_\infty$		$k.\ 10^3$	
(min.)	(1)	(2)	(1)	(2)
0	4·50°	4·40°	—	—
5	4·20	4·10	6·0	6·1
12	3·82	3·72	5·9	6·1
20	3·39	3·31	6·0	6·2
30	2·92	2·86	6·3	6·4
45	2·37	2·30	6·2	6·3
65	1·74	1·72	6·3	6·3
			6·1	6·2

Table 7.

Sodium chloride $v = 1$.

t	$a - a_\infty$		$k.\ 10^3$	
(min.)	(1)	(2)	(1)	(2)
0	4·55°	3·87°	—	—
5	4·26	3·61	5·7	6·0
12	3·86	3·29	6·0	5·9
20	3·47	2·95	5·9	5·9
30	3·04	2·55	5·8	6·0
45	2·43	2·07	6·0	6·0
65	1·87	1·57	5·9	6·0
			5·9	6·0

Thus, in the dilution of 15, the action of the neutral salt is not noticeable. It is, however, remarkable in the dilution of 10, and increases gradually as the dilution is lowered; indeed, the action is negative as found by Levy and Trey.

3. Catalytic Action of a Neutral Salt in Presence of the Free Acid.

On experimenting with hydrochloric acid (0·1*n.*) and sodium chloride, Trey[1] came to the conclusion that a small quantity (0·1*n.*) of the neutral salt augments the action of the acid; but that its greater quantity (0·2*n.*) diminishes it. The author has remarked in the previous paper, that the latter part of Trey's conclusion could not be drawn from his experimental data. This contention comes from the fact that Trey did not take into consideration the end values of the observations, which were not always the same. The following experiments were undertaken to make this relationship clear.

[1] Loc. cit.

Table 8.

Hydrochloric acid $v=15$.

	(1)			(2)	
t	$a-a_\infty$	$k.\ 10^2$	t	$a-a_\infty$	$k.\ 10^2$
0	3·09°	—	0	3·61°	—
3	2·75	1·67	4	3·06	1·78
7	2·33	1·75	8	2·62	1·74
11	1·97	1·78	12	2·22	1·76
15	1·68	1·76	16	1·89	1·75
19	1·44	1·75	20	1·62	1·74
		1·74			1·75

Table 9.

Hydrochloric acid $v=15$, Sodium chloride $v=15$.

t	$a-a_\infty$			$k.\ 10^2$		
(min.)	(1)	(2)	(3)	(1)	(2)	(3)
0	3·33°	3·52°	3·29°	—	—	—
3	2·95	3·12	2·91	1·75	1·74	1·78
7	2·54	2·67	2·49	1·68	1·71	1·73
11	2·16	2·25	2·10	1·71	1·77	1·77
15	1·79	1·92	1·79	1·79	1·75	1·76
19	1·55	1·64	1·56	1·75	1·75	1·70
				1·74	1·74	1·75

Table 10.

Hydrochloric acid $v=15$, Sodium chloride $v=10$.

t	$a-a_\infty$			$k.\ 10^2$		
(min.)	(1)	(2)	(3)	(1)	(2)	(3)
0	3·25°	3·17°	3·39	—	—	—
3	2·88	2·81	3·00	1·75	1·77	1·77

t	$a-a_\infty$			$k.\ 10^2$		
(min.)	(1)	(2)	(3)	(1)	(2)	(3)
6	2·57	2·48	2·67	1·70	1·78	1·73
9	2·27	2·20	2·36	1·73	1·76	1·75
12	1·99	1·96	2·08	1·77	1·74	1·77
15	1·78	1·74	1·84	1·74	1·74	1·77
				1·74	1·76	1·76

Table 11.

Hydrochloric acid $v=15$, Sodium chioride $v=5$.

t	$a-a_\infty$			$k.\ 10^2$		
(min.)	(1)	(2)	(3)	(1)	(2)	(3)
0	2·98°	3·74°	3·16°	—	—	—
3	2·63	3·29	2·78	1·81	1·86	1·86
6	2·35	2·92	2·45	1·72	1·79	1·84
9	2·06	2·59	2·12	1·78	1·77	1·93
12	1·79	2·27	1·91	1·85	1·81	1·82
15	1·58	2·00	1·71	1·84	1·82	1·78
				1·80	1·81	1·85

Table 12.

Hydrochloric acid $v=15$, Sodium chloride $v=3$.

t	$a-a_\infty$			$k.\ 10^2$		
(min.)	(1)	(3)	(3)	(1)	(2)	(3)
0	3·98°	3·05°	3·92°	—	—	—
3	3·51	2·68	3·45	1·80	1·87	1·85
6	3·07	2·36	3·04	1·88	1·86	1·84
9	2·69	2·09	2·68	1·89	1·82	1·84
12	2·41	1·81	2·38	1·82	1·88	1·81
15	2·11	1·59	2·14	1·84	1·89	1·75
				1·85	1·86	1·82

Table 13.

Hydrochloric acid $v=15$, Sodium chloride $v=1$.

t	$a-a_\infty$			$k.\ 10^2$		
(min.)	(1)	(2)	(3)	(1)	(2)	(3)
0	3·14°	3·65°	3·66°	—	—	—
3	2·74	3·19	3·21	1·97	1·95	1·90
6	2·43	2·79	2·80	1·85	1·78	1·95
9	2·08	2·46	2·49	1·99	1·90	1·86
12	1·85	2·10	2·13	1·91	2·00	1·96
15	1·61	1·88	1·88	1·94	1·92	1·92
				1·93	1·91	1·92

The results may be summarised in the following table:—

Table 14.

Dilution.		$k.\ 10^2$	Dilution.		$k.\ 10^2$
Hydrochloric acid.	Sodium chloride.		Hydrochloric acid.	Sodium chloride.	
—	1	0·59	15	—	1·74
—	5	0·62	,,	15	1·74
—	10	0·63	,,	10	1·75
—	15	0·66	,,	5	1·82
—	—	0·66	,,	3	1·84
			,,	1	1·92

Thus, in a solution of hydrochloric acid by the dilution of 15, the presence of sodium chloride exerts no remarkable influence, provided the dilution is higher than 10. By the dilution of 5, the influence of the neutral salt becomes noticeable, increasing with the concentration, and accelerating the action of the hydrogen ions, as is the case with most of the hydrogen ion catalyses. It demands special notice, however, that sodium chloride,

which retards the velocity of the reaction when present alone, should accelerate it in presence of the free acid.

4. Catalytic Action of a Weak Acid.

According to Levy[1] the velocity of the retrogression of the rotatory power of d-glucose is said to be accelerated by 1/5 and 1/10 *n.* acetic acid and by 1/10 *n.* propionic acid; Trey,[2] on the contrary, came to the conclusion that 1/10 *n.* acetic acid and propionic acid retard the velocity. Trey's conclusion is, however, hardly possible of inference from his experimental data, as the author pointed out in the previous paper.

The catalytic action of the hydroxyl ion on the reaction is very strong, while that of the hydrogen ion is comparatively weak. It is, therefore, considered that the hydroxyl ions from water may play a prominent part in the reaction in an aqueous solution to which no special catalyser is added. In an acid solution, the concentration of the hydroxyl ions is naturally very low, and the catalytic action of the hydrogen ions, present in a comparatively high concentration, is possibly predominant. If the concentration of the acid solution be gradually diminished, however, we might arrive at a state in which the catalytic action of the hydrogen ions is no longer significant, while the concentration of the hydroxyl ions is still far less than in a pure aqueous solution. In such cases the acid would act negatively, its presence retarding the velocity of the reaction. On further dilution of the acid, the concentration of the hydroxyl ions will increase and the velocity of the reaction will tend to equal that in a pure aqueous solution. It is expected that such a relationship may be arrived at in not too high dilutions, if we work with weak acids. Acetic and succinic acids were taken for the verification of that relationship, with the following results:

[1] Loc. cit.
[2] Loc. cit.

Acetic acid.

Table 15.

	$v=10$.		$v=20$.	
t	$a-a_\infty$	$k.\ 10^3$	$a-a_\infty$	$k.\ 10^3$
0	4·17°	—	4·27°	—
5	3·85	6·9	3·96	6·5
12	3·44	7·0	3·53	6·9
20	3·01	7·1	3·14	6·7
30	2·58	7·0	2·68	6·7
45	2·04	6·9	2·10	6·9
65	1·50	6·8	1·56	6·7
		6·9		6·7

Table 16.

$v=30$.

t	$a-a_\infty$		$k.\ 10^3$	
(min.)	(1)	(2)	(1)	(2)
0	4·35°	4·61°	—	—
5	4·03	4·27	6·6	6·7
12	3·65	3·84	6·4	6·6
20	3·21	3·41	6·6	6·6
30	2·77	2·95	6·5	6·5
45	2·18	2·35	6·7	6·5
65	1·60	1·71	6·6	6·6
			6·6	6·6

Table 17.

$v=75$.

t	$a-a_\infty$		$k.\ 10^3$	
(min.)	(1)	(2)	(1)	(2)
0	4·86°	4·35°	—	—
5	4·51	4·03	6·5	6·6
12	4·04	3·61	6·7	6·7

t	$a-a_\infty$		$k.\ 10^3$	
(min.)	(1)	(2)	(1)	(2)
20	3·57	3·23	6·7	6·5
30	3·08	2·78	6·6	6·5
45	2·45	2·19	6·6	6·6
65	1·82	1·68	6·6	6·4
			6·6	6·6

Table 18.

$v=150.$

t	$a-a_\infty$		$k.\ 10^3$	
(min.)	(1)	(2)	(1)	(2)
0	4·26°	4·26°	—	—
5	3·98	3·96	5·9	6·3
12	3·57	3·56	6·4	6·5
20	3·19	3·17	6·3	6·4
30	2·73	2·72	6·4	6·5
45	2·18	2·19	6·5	6·4
65	1·62	1·61	6·4	6·5
			6·3	6·4

Table 19.

$v=300.$

t	$a-a_\infty$		$k.\ 10^3$	
(min.)	(1)	(2)	(1)	(2)
0	4·46°	4·56°	—	—
5	4·16	4·23	6·0	6·5
12	3·74	3·84	6·0	6·2
20	3·32	3·39	6·4	6·4
30	2·87	2·95	6·4	6·3
45	2·29	2·36	6·4	6·4
65	1·69	1·73	6·5	6·5
			6·4	6·4

Table 20.

$v = 600.$

t	$a - a_\infty$		$k.\ 10^3$	
(min.)	(1)	(2)	(1)	(2)
0	4·21°	4·59°	—	—
5	3·89	4·26	6·9	6·5
12	3·51	3·83	6·6	6·6
20	3·12	3·37	6·5	6·7
30	2·67	2·91	6·6	6·6
45	2·17	2·31	6·4	6·5
65	1·60	1·70	6·5	6·6
			6·6	6·6

Succinic acid.

Table 21.

$v = 100.$

t	$a - a_\infty$		$k.\ 10^3$	
(min.)	(1)	(2)	(1)	(2)
0	4·29°	4·44°	—	—
5	3·97	4·12	6·7	6·5
12	3·54	3·69	6·9	6·7
20	3·10	3·22	7·0	7·0
30	2·67	2·80	6·9	6·7
45	2·13	2·23	6·8	6·7
65	1·56	1·61	6·8	6·8
			6·8	6·7

Table 22.

$v = 200$.

t	$a - a_\infty$		$k.\ 10^3$	
(min.)	(1)	(2)	(1)	(2)
0	4·66°	4·08°	—	—
5	4·32	3·79	6·6	6·4
12	3·89	3·41	6·5	6·5
20	3·46	3·01	6·5	6·0
30	3·00	2·59	6·4	6·6
45	2·39	2·07	6·5	6·5
65	1·73	1·52	6·6	6·6
			6·5	6·5

Table 23.

$v = 300$.

t	$a - a_\infty$		$k.\ 10^3$	
(min.)	(1)	(2)	(1)	(2)
0	4·58°	4·41°	—	—
5	4·26	4·11	6·3	6·1
12	3·86	3·71	6·2	6·3
20	3·44	3·29	6·2	6·4
30	2·95	2·83	6·4	6·4
45	2·35	2·27	6·4	6·4
65	1·77	1·67	6·4	6·5
			6·3	6·4

Table 24.

$v = 600$.

t	$a - a_\infty$		$k.\ 10^3$	
(min.)	(1)	(2)	(1)	(2)
0	4·70°	4·30°	—	—
5	4·38	3·99	6·1	6·5

t	$a-a_\infty$		$k.\ 10^3$	
(min.)	(1)	(2)	(1)	(2)
12	3·93	3·60	6·5	6·4
20	3·48	3·19	6·5	6·5
30	3·01	2·72	6·5	6·6
45	2·43	2·15	6·4	6·6
65	1·79	1·58	6·4	6·6
			6·4	6·5

Table 25.

$v = 1200.$

t	$a-a_\infty$		$k.\ 10^3$	
(min.)	(1)	(2)	(1)	(2)
0	4·13°	4·40°	—	—
5	3·85	4·07	6·1	6·8
12	3·45	3·67	6·5	6·6
20	3·09	3·28	6·3	6·4
30	2·63	2·82	6·5	6·4
45	2·09	2·26	6·6	6·4
65	1·56	1·67	6·5	6·5
			6·4	6·5

Thus, the experiments confirm the author's expectations. As seen from the tables, the dilution, in which the minimum velocity is observed, is higher with succinic acid than with acetic acid. The fact, so far as it is concerned, is in harmony with theory, as succinic acid is stronger than acetic acid, the affinity constants at 25° being in the ratio of 3·7 to 1.

Summary.

1. The influence of temperature on the velocity of the retrogression of the rotatory power of d-glucose was studied.

2. Sodium chloride by dilutions lower than 10 retards the velocity.

3. In the presence of hydrochloric acid ($v = 15$), sodium chloride by dilutions lower than 10 augments the catalytic action of the hydrogen ions, but exerts no influence in the dilution of 10.

4. The catalytic action of a weak acid may be negative; that is, in its presence in certain dilutions, the velocity is less than in a pure aqueous solution. The view was theoretically deduced and verified by experiments.

Kinetics of the Hydrolytic Decomposition of Methyl Acetate by the Catalytic Action of Acetic Acid.

By

Kozo Ikawa.

With regard to the conversion of ammonium cyanate into urea, J. Walker and Kay[1] once determined the velocity of reaction by measuring the electrolytic conductivity of its solution at stated intervals. Since then, Walker[2] has shown that such a procedure is capable of wider application, by actually utilizing it, with satisfactory results, to the determination of the velocities of saponification of an ester by a caustic alkali.

In the classical work of W. Ostwald[3] on the hydrolytic decomposition of esters by the catalytic action of acids, he obtained a result in which the velocity coefficient decreases gradually with time, by using acetic acid as a catalyser. With such a weak catalyser, a considerable period of time is needed, and the inconstancy of the velocity coefficient is ascribed to the loss of the ester by evaporation during the experiment. In a case where the reaction system can remain perfectly closed during the experiment, Walker's method of measurment may be conveniently applied. At the suggestion of Professor Osaka, the author has undertaken an investigation of the subject and the results obtained will be stated below.

Let a be the initial concentration of acetic acid, b that of methyl acetate, $a+x$ and $b-x$ those at the time, t, respectively, K the dissociation constant of acetic acid, and γ its dissociation degree.

[1] Journ. Chem. Soc. **71**, 489, (1897).
[2] Chem. News **94**, 138, (1906).
[3] Journ. f. prak. Chem. (2), **28**, 481, (1883.)

We have, then, for the electrolytic dissociation of acetic acid at the time t:—

$$K(1-\gamma)(a+x)=\gamma^2(a+x)^2.$$

As the concentration of the acetic acid used was about 1 normal, γ may be neglected against 1, and we have:

$$K(a+x)=\gamma^2(a+x)^2.$$

Since the specific conductivity $\varkappa$ of the solution may be approximately proportional to the concentration of the dissociated acetic acid, we have:

$$\varkappa=c\sqrt{K(a+x)}=K'\sqrt{a+x},$$

when c and K' are constants.

If $\varkappa_0$ be the specific conductivity of the solution at the initial time, $\varkappa$ be one at the time t, and $\varkappa_\infty$ one at the end of the reaction, then we have:—

$$\varkappa_0=K'\sqrt{a},$$
$$\varkappa=K'\sqrt{a+x},$$
$$\varkappa_\infty=K'\sqrt{a+b}.$$

Now, the velocity of hydrolysis may be expressed by:—

$$\frac{dx}{dt}=k\gamma(a+x)(b-x),$$

or

$$\frac{dx}{dt}=k\sqrt{K(a+x)}(b-x),$$

where k is the velocity coefficient of the reaction. On integrating it gives:—

$$k\sqrt{K(a+b)}=\frac{1}{t}\ln\frac{(\sqrt{a+b}-\sqrt{a})(\sqrt{a+b}+\sqrt{a+x})}{(\sqrt{a+b}+\sqrt{a})(\sqrt{a+b}-\sqrt{a+x})}.$$

On expresssing the concentrations in terms of the specific conductivities, we have:—

$$k\sqrt{K(a+b)}=\frac{1}{t}\ln\frac{(\varkappa_\infty-\varkappa_0)(\varkappa_\infty+\varkappa)}{(\varkappa_\infty+\varkappa_0)(\varkappa_\infty-\varkappa)},$$

or

$$0{\cdot}4343k\sqrt{K(a+b)}=\frac{1}{t}\log\frac{(\varkappa_\infty-\varkappa_0)(\varkappa_\infty+\varkappa)}{(\varkappa_\infty+\varkappa_0)(\varkappa_\infty-\varkappa)}.$$

Since the left side of the equation is constant for a given solution, the right side should be, of course, the same, and the verification of such a relation was the object of the present investigation.

The experiments were carried out as follows: A cylindrical glass vessel was used, the inside of which was covered with pure paraffin in order to prevent the dissolution of glass: 50 c. c. of 1 normal acetic acid, freshly prepared, and 5 c. c. of methyl acetate were introduced into the vessel, which was closed with a paraffined cork carrying the parallel horizontal electrodes, and then the vessel was dipped into a thermostat at 25°. The conductivity of the solution was then measured by the usual method. Since the resistance in the rheostat was kept constant at 150 ohms all the time, the relative conductivity of the solution, as indicated by the ratio of the two parts of the measuring bridge, divided by the knife-edge contact, instead of the specific conductivity, was employed in the calculation.

The results were as follows:—

Table 1.

t (hours.)	Reading on the measuring bridge.	Relative conductivity.	$0{\cdot}4343k\sqrt{K(a+b)} \times 10^3$
0	39·96	1·502	—
73	38·84	1·575	0·95
95	38·53	1·595	0·91
140	38·00	1·632	0·89
145	37·95	1·635	0·89
165	37·74	1·650	0·90
169	37·69	1·654	0·90
213	37·21	1·687	0·88
217	37·19	1·689	0·88
230	36·98	1·704	0·91
240	36·95	1·707	0·88
260	36·80	1·717	0·87

t (hours.)	Reading on the measuring bridge.	Relative conductivity.	$0{\cdot}4343k\sqrt{K(a+b)}$ $\times 10^3$
313	36·20	1·762	0·92
337	35·86	1·789	0·97
361	35·74	1·798	0·95
440	35·12	1·847	0·97
475	34·91	1·864	0·98
521	34·75	1·878	0·94
545	34·72	1·880	0·91
566	34·46	1·902	0·97
617	34·25	1·919	0·96
665	34·06	1·936	0·97
713	33·83	1·956	0·99
∞	32·41	2·085	—

Table 2.

t (hours.)	Reading on the measuring bridge.	Relative conductivity.	$0{\cdot}4343k\sqrt{K(a+b)}$ $\times 10^3$
0	42·10	1·375	—
25	41·70	1·398	0·85
48	41·35	1·418	0·85
75	40·90	1·445	0·90
96	40·60	1·463	0·90
121	40·34	1·479	0·86
169	39·75	1·516	0·87
192	39·46	1·534	0·87
240	38·94	1·568	0·88
264	38·70	1·584	0·88
284	38·51	1·596	0·89
335	38·05	1·629	0·89
350	37·84	1·643	0·91
375	37·60	1·660	0·94

t (hours.)	Reading on the measuring bridge.	Relative conductivity.	$0{\cdot}4343k\sqrt{K(a+b)} \times 10^2$
408	37·40	1·674	0·92
432	37·23	1·686	0·92
530	36·49	1·741	0·97
576	36·28	1·756	0·96
610	36·10	1·770	0·97
625	36·04	1·775	0·97
840	35·35	1·829	0·96
∞	34·15	1·928	—

As shown by these tables, the results are satisfactory when it is taken into account that the reaction in question took such a long period of nearly four months to come practically to its end.

April, 1908.

Physico-chemical Studies on Tofu.

By

Yogoro Kato.

In this country, a preparation called *tofu*, from *soya*-beans, is in common use for the table. It is made as follows: the beans are soaked in water until they swell. They are then ground and water is added, a milky solution[1] being thus obtained. This solution is boiled and filtered when hot in order to separate the skins. To the filtrate, which has an appearance quite similar to that of milk, a bitter salt solution is added to coagulate it and facilitate the separation of the *tofu*-making part from water in the next step of the process. This bitter salt solution is obtained as the residue in making common salt from sea-water by evaporation. The coagulated portion is filtered through cloth laid inside a box having several holes in its sides and bottom: this box also serves the further purpose of moulding the *tofu* into desired shape. The whole contents of the box is strained and thus there is obtained a white and soft rectangular mass having somewhat the appearance of jelly, yet being more tender. This is cut into smaller rectangular pieces and kept under water without danger of breaking: one of these pieces is called one *chô*.

S. Inoue[2] investigated the composition of *tofu* and came to the conclusion that it is a chemical compound of casein from the bean with calcium and magnesium in the bitter salt solution. This conclu-

[1] Strictly speaking, this is not a solution, but water containing insoluble matter in suspension: the word is used only for convenience.

[2] Bull. Agr. Coll. Tokyo Imp. Univ. 2, 209, (1895).

sion was reached upon detecting calcium and magnesium salts in the solution obtained by treating the *tofu* with a dilute solution of acetic acid.

Now that our knowledge concerning the properties of colloid is much advanced, interesting results were promised on taking up the matter from a new point of observation. The *soya*-bean contains a large quantity of albumen. According to Inoue, the milky solution, obtained as stated, was found to have a composition similar to that of milk; i. e., to contain nitrogenous matter, fat, and other constituents as much as those in milk. It is well known that albumen forms colloid: it is also well known that colloid is generally coagulated by an electrolyte having cation of high valency and that the increase of valency in the cation of the electrolyte enhances the capacity for coagulation. The size of the colloidal particle is very different according to its nature. In some cases, the order of its diameter is that of the wave-length of light; and in others, it is easily seen under a microscope of low power. The milky solution obtained after grinding the soaked *soya*-beans was found under a microscope of low power to consist of white particles in suspension. Thus the solution is, in a proper sense, a colloidal suspension; and consequently the preparation of *tofu* may be based upon the coagulation of the colloid by electrolytes.

In the present memoir, the problem is studied by both chemical and physical methods.

I. CHEMICAL STUDIES.

A. Washing the *Tofu* with Distilled Water.

It will be interesting to see if the calcium and the magnesium in the *tofu* come out upon simple washing with distilled water. If *tofu* is a chemical compound of casein with calcium and magnesium, it may not be easy to wash them out with water.

Moreover, the *tofu* itself must dissolve, if calcium and magnesium are dissolved out with water. As a preliminary test, one *cho* of *tofu* was crushed by hand and decanted four times with distilled warer, filtered, dried at 110° in an air-bath, and weighed. The weighed residue was ignited and again weighed. The results were as follows:—

Residue	16·78 gr.
Ash	0·57 gr. (3·4% of residue).

The ash was found to contain phosphoric acid, calcium, magnesium, iron, aluminium, and silica.

Two *chô* of *tofu* were crushed and decanted ten times with distilled water. Residue and ash were determined as in the previous case, the results being as follows:—

	Residue.	Ash.
1.	25·19 gr.	0·602 gr. (2·4% of residue).
2.	19·02 gr.	0·330 gr. (1·8% of residue).

The ash was treated with nitric acid. Phosphoric acid was precipitated from the solution with a nitric acid solution of ammonium molybdate and determined as magnesium pyrophosphate in the usual manner. From the filtrate, oxides of iron and aluminium were determined by precipitation with ammonia. Again, from the filtrate calcium was precipitated as oxalate, and magnesium as ammonium magnesium phosphate. The result was as follows:—

	P_2O_5	Fe_2O_3 and Al_2O_3	CaO	MgO
1.	30·0%	traces	—	1·98%
2.	43·7%	traces	9·7%	2·4%

Now, it is interesting to note the quantity of magnesium and calcium oxides by comparison with the residue other than with the ash, the quantity of residue being taken as 100:—

	P_2O_5	CaO	MgO
1.	0·72	—	0·049
2.	0·73	0·165	0·048

From this it seems evident that calcium and magnesium can hardly be called chemical constituents of *tofu*.

B. Washing with Dilute Hydrochloric Acid Solution.

By experiments, the *tofu* solution was found to be coagulated upon the addition of a dilute solution of hydrochloric acid; therefore, even if *tofu* is a chemical compound of casein with calcium and magnesium, it may be decomposed and calcium and magnesium washed out with a dilute hydrochloric acid solution without much change in its form. If calcium and magnesium exist in *tofu*, forming a compound with phosphoric acid or its derivative[1] insoluble in water, they may be dissolved out by a dilute solution of hydrochloric acid more readily than with water.

Two *chô* of *tofu* were crushed and allowed to remain over night in a dilute hydrochloric acid solution (2%): it was then washed with water by decantation seven or eight times. The residue and the ash were weighed, as in the previous experiments. The phosphoric acid and the oxides of calcium and magnesium in the ash were also determined in the same way. The result was as follows:—

	Residue.	Ash.
1.	17·50 gr.	0·0800 gr. (0·45% of residue).
2.	29·36 gr.	0·0758 gr. (0·24% of residue).

Composition of ash:—

	P_2O_5	CaO	MgO
1.	43%	—	traces
2.	41%	11%	traces

From this it is manifest that the ash was much diminished by washing with the hydrochloric acid solution. It is difficult to determine, from this result, whether or not *tofu* is a chemical

[1] For the presence of the derivative, refer to Funazu, Bull. Agr. Coll. Tokyo Imp. Univ. 7, 458.

compound of casein with calcium and magnesium; but the diminution of the ash, upon being treated with a dilute hydrochloric acid solution, may be ascribed to the decomposition of the calcium and the magnesium salts of phosphoric acid, or its derivative, which exist in *tofu*.

A Comparison of the Results of Washing with Water and with Hydrochloric Acid Solution.

In the following table, both results are summarized for the purpose of comparison.

		Wt. of residue.	Ash in residue.	Composition of ash. P_2O_5	CaO	MgO
1.	Washed with water.	16·78 gr.	3·4%	—	—	—
2.	,,	25·19	2·4	30·0%	—	1·98%
3.	,,	19·02	1·79	43·7	9·7%	2·4
1.	Treated with dilute HCl. sol.	17·50	0·45	43·0	—	traces
2.	,,	29·36	0·24	41·0	11·0%	traces

As has already been mentioned, the reduction of ash by washing with a hydrochloric acid solution is clearly indicated. Moreover, the composition of the ash obtained does not seem to be materially affected by the difference in the method of treating the residue, though more experiments are needed for a decisive conclusion. If it is proved to be so, it may mean that the calcium (and the magnesium) in *tofu* forms a compound with phosphoric acid or its derivative. The decrease of ash upon washing with hydrochloric acid solution may mean simply that the salt is dissolved out. Above all, it hardly looks as if *tofu* is a chemical compound of casein with calcium and magnesium.

II. PHYSICAL STUDIES.

A. Behaviour of the *Tofu* Solution toward an Electric Current.

It is well known that albumens form negative colloids in an

acidic solution and positive ones in a neutral. The *tofu* solution is acidic to a test paper, and may be expected to contain the negative colloid. A *tofu* solution was placed in a U-tube and a current of 110 volts pressure applied. After a few minutes, coagulation was observed about the anode; the solution near the cathode becoming almost clear. This shows that the *tofu* solution contains the negative colloid. As has been already explained, the *tofu* solution is prepared by filtering hot that which is obtained by grinding soaked *soya*-beans with the addition of water. A similar experiment was made with the *tofu* solution which had been prepared from beans soaked in distilled water, in grinding, and filtering without previous heating. A similar phenomenon to that which has just been described was observed. Hence, heating seems to have no effect on the solution with respect to its behaviour toward the current.

B. Coagulation by Electrolytes.

The result of the described experiment demonstrates that the *tofu* solution contains a negative colloid, and it may be expected to be coagulated by electrolytes containing higher valent cation. By experiments, it was found that it is not easy to determine accurately when the colloid begins to coagulate upon the addition of an electrolyte, owing to its milky appearance. Hence, no care was taken to dialyze the solution beforehand: the presence of impurities may, as a matter of fact, interfere with the experiments; but the error due to the difficulty of determining the beginning of the coagulation, seemed to be greater than that arising from the interference mentioned. Notwithstanding, it was desirable to study the actual coagulation in the manufacture of *tofu*.

A *tofu* solution was diluted with three times its volume of water. 50 c. c. of this diluted solution was heated to the boiling-point in a beaker and the electrolyte added until a distinct separation was observed.

The result was as follows:—

	Concentration (formula weight in 1 lit.)	Quantity of electrolyte required.
KCl	1	No separation was observed.
$\frac{1}{2}MgCl_2$	$^1/_{50}$	21 c.c.
$^1/_6\ Al_2(SO_4)_3$	$^1/_{100}$	23 c.c.

Thus demonstrating that an electrolyte having a higher-valent cation has greater capacity for coagulating the colloid in the *tofu* solution.

Summary and Conclusion.

Tofu was washed with water and with a dilute solution of hydrochloric acid. The quantity of ash was found to be so small, when compared with the volume of the residue from which it had been obtained, that it seems highly probable calcium and magnesium do not exist in *tofu* as its essential constituents. On the contrary, they—especially calcium—appear to be forming the salt of phosphoric acid or its derivative.

The behaviour of the *tofu* solution toward an electric current, and also its microscopic appearance, were studied. It was found to have the characteristics of a negative colloid, or—more properly speaking—to belong to that class of solutions which might be called colloidal suspension. Then the action of electrolytes upon the solution was studied and found to be quite similar to that which had been observed in the cases of other colloids.

Finally, it seems quite probable that the manufacture of *tofu* is based upon the coagulation of the colloid by electrolytes: consequently, several electrolytes containing cation of high valency, besides calcium and magnesium, may be employed for the coagulation.

Chemical Laboratory,
Higher Technological School of Tokyo.

The Electrical Conductivity and Dissociation of Sulphuric acid in Aqueous Solutions at Higher Temperatures.

By

Yogoro Kato.

At the temperatures higher than 25°, very few accurate measurements have hitherto been made of electrical conductivity, though it forms an important basis for studying the chemical as well as the physical properties of solutions at those temperatures. Prof. Noyes and his co-workers undertook the measurement in the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology; and a publication, entitled "The Electrical Conductivity of Aqueous Solutions" has been issued by the Carnegie Institution of Washington: it is a resumè of the work carried on in the aforesaid laboratory. The investigations discussed in the present memoir were also carried out in that laboratory: the electrical conductivity of the aqueous solution of sulphuric acid at 18°, 100°, 156°, and 218° was measured, and the degree of electrolytic dissociation was calculated therefrom.

Apparatus used in the Investigation.

The cell employed for introducing the solution for the purpose of measuring the electrical conductivity was the bomb devised for that purpose by Noyes and Coolidge: it was essentially a cylindrical vessel made of soft crucible steel, the inner surface lined with sheet platinum which served as one electrode: the other electrode was a platinized platinum-iridium cylinder fixed at the bottom and insulated from the former by means of a

quartz tube and mica; the cover joint was made tight by means of a pure gold ring. For further details, reference should be made to the inventors' papers.[1]

The heaters of the bomb were different, according to the temperature at which the measurement was conducted; at 18° and 100° xylene baths were used; at 156° a vapour bath of brombenzene, and at 218° one of naphthalene.

The thermometers employed for the measurement at 18° and 100° were Beckmann's: that for 180° was compared with a standard thermometer, and that for 100° was tested by heating with steam in Regnault's apparatus after each measurement. The thermometer used for measuring 156° and 218° was a French one made by Alverguist; its 100° point was determined as usual, and the naphthalene point by using naphthalene purified as suggested by Crafts[2] taking Taquerrod and Wassmer's value[3] for the boiling-point: the interval between the two points was calibrated by the method recommended by Crafts, and reduced to the hydrogen-gas scale by adopting his correction. The naphthalene point was tested several times during the investigation.

The conductivity was measured by Kohlrausch's well known method: the apparatus employed was of the roller type, as described by Kohlrausch and Holborn,[4] furnished by Hartmann and Braun: the slide wire was calibrated by Strohal and Barus' method;[5] the resistance coils were of manganine, and were compared with standard resistance certificated by the Deutsche physikalisch-technische Reichsanstalt.

Preparation of the Solution.

"Strictly chemically pure sulphuric acid," furnished by Baker

[1] A. A. Noyes and W. D. Coolidge: The Elect. Conductivity 9; Proc. Amer. Acad. Arts and Sciences, **39**, 165 (1903); Zeitchr f. physik. Chem., **46**, 323 (1903); Journ. Amer Chem. Soc., **26**, 134 (1904).
[2] Amer. Chem. Journ. **5**, 307 (1887).
[3] Journ. chim. phys., **2**, 72 (1904).
[4] Leitvermogen d. Elektrolyte, 1898, 42.
[5] Ibid. 45.

and Adamson, was used to prepare a fifth normal stock solution. The concentrated acid (10 c. c. portions being taken usually) was tested for arsenic with hydrogen sulphide; for nitric acid with diphenylamine; for nitrous acid with starch and potassium iodide; for hydrochloric acid with silver nitrate; for selenium with ferrous sulphate; and for ammonia with Nessler solution: it was found that none of the impurities was present in appreciable quantity. The stock solution was diluted with conductivity water in order to prepare solutions of different concentration. The conductivity water was obtained by re-distilling ordinary distilled water with the addition of an alkaline solution of potassium permanganate, and collecting it at almost boiling-point in a "Non-sol" bottle furnished by Tatum & Co.: conductivity water having a specific conductivity of $0{\cdot}5 \times 10^{-6}$ at 18° was easily obtained thus. In preparing the solutions, the stock solution and the water were taken by weight, using a weighing burette.

The concentration of the stock solution was determined on August 11–15, 1905, by two independent methods: i. e., first, as barium sulphate; second, by titrating it with phenolphthalein against a pure sodium hydroxide solution which was standardized also with the same indicator againt a hydrochloric acid solution whose concentration was determined as silver chloride. Again, the concentration was determined by Noyes and Eastman on December 9, 1905, by using an ignited pure sodium carbonate. To a solution of known weight of the carbonate, a slight excess of the sulphuric acid solution was added and boiled, then the excess was titrated by a solution of potassium hydroxide with phenolphthalein. The results were as follows:—

1.	As $BaSO_4$	110·43
2.	Against HCl	110·70
3.	Against Na_2CO_3	110·71
		110·61

The concentration is expressed by the number of millimols of

H_2SO_4 in one kilogramme of the solution, correcting the weights to vacuo.

Conductance-capacity of the Bomb.

The conductance capacity of the bomb at 18° is the factor by which the observed conductance must be multiplied to give the specific conductance at the temperature. It was determined by 0·01 normal solutions of ignited potassium and sodium chlorides purified by hydrochloric acid, applying the correction for the conductivity of water used in their preparation. The values adopted for the equivalent conductance of these salts are those given by Kohlrausch and Maltby[1] i. e, 122·43 and 101·95 respectively. The results were as follows:—

Date (1905).	Salts.	Conductance $\times 10^6$	Conductance capacity. Separate values.	Conductance capacity. Final values.
Aug. 17	KCl	8·195	0·14939	0·14934
Aug. 17	NaCl	6·829	0·14929	
Aug. 29	KCl	8·201	0·14928	0·14923
Aug. 29	NaCl	6·834	0·14918	

The first three values for the conductance are the means of two separate determinations which were almost concordant.

The conductance capacity at other temperatures is to be determined from the expansion of the bomb, the inner electrode and quartz tube. But Noyes and Melcher[2] found by experiment that the only significant factor determining the change, was the expansion of the platinum-iridium electrode. The computation shows that the conductance-capacity at 18° should be decreased by the following percentages:—

100°	156°	218°
0·10	0·18	0·26

[1] See Landolt-Bernstein-Meyerhoff, Tabellen, 1905, 744.

[2] The Electrical Conductivity, 74.

Method of Procedure.

To avoid the effect of absorption of the solution by the electrode, the solution was allowed to remain in the bomb between experiments, and the bomb was rinsed with the fresh solution just before introducing it. Moreover, before the first introduction of the solution, the bomb was boiled with it, to avoid contamination of the solution from any impurity that might have been absorbed by the electrode. The volume of the solution in the bomb at 218° was 120 c. c., so that the vapour-space left above the solution did not exceed 1–2 c. c. The vapour occupying this space could not, therefore, cause much error in the concentration of the solution, and, consequently, no correction was applied for this error.

At 18° the bomb was introduced into the xylene bath after having been shaken. When a constant reading on the slide-wire was reached, the bomb was taken out from the bath and again shaken well: then it was put back into the bath again, and the conductance was measured. At 100° or higher temperatures, the bomb was introduced into the bath, which had been heated to that temperature, and when the bomb had become heated to that temperature, it was taken out and well shaken, and then put back into the bath and the conductance measured. In measuring the conductance at a given temperature, three different resistance-coils were used; the mean of these three values being taken as the desired conductance.

Water Correction.

The presence of carbonic acid as an impurity in the conductivity water used in the preparation of the solution, is to increase the conductance of sulphuric acid: but the error caused by its presence in a solution of strong acid, such as sulphuric acid, must be very small when compared with conductance in water. Even if they had the same conductance in the solution as in conductivity water, the correction required for it hardly amounted

to 0·2 per cent. in a 0·5 milli-equivalent solution: therefore no correction was applied for this.

Conductivity Data.

The concentration at different temperatures was calculated from that at 4°, by dividing it by the following numbers:—

18°	100°	156°	218°
1·0014	1·0431	1·0980	1·1862

In table 1, the second column gives the concentration in milli-equivalents per litre referred to the equivalent weight of oxygen as 8·00, and the weights being reduced to vacuo; the fourth column, the concentration at the temperature calculated as given above; the fifth, the measured conductance in reciprocal ohms, correction having been applied for the errors in the slide-wire, resistance-coils, and leads, but not for the impurities in the water; and the sixth, the equivalent conductance calculated from the conductance given in the fifth column, the concentration in the fourth column, and the value of the conductance-capacity.

Table 1.—Conductivity Data for Sulphuric Acid.

Date (1905).	Concentration at 4°.	Temperature t°	Concentration at t°.	Conductance $\times 10^6$	Equivalent conductance.
Aug. 23	11·748	18 00	11·733	23,660	301·2
"	"	155·9	10·707	34,460	479·9
"	"	217·4	9·913	35,790	537·9
"	"	18·00	11·733	23,920	304·5
Aug. 24	11·762	18·00	11·747	23,810	302·8
"	"	99·83	11·279	33,044	437·1
"	"	155·9	10·720	34,300	477·2
"	"	217·5	9·924	35,360	533·9
"	"	18·00	11·747	24,020	305·4
Sept. 14	11·643	18·00	11·627	23,720	304·5

Table I.—*Continued.*

Date (1905).	Concentration at 4°.	Temperature t°	Concentration at t°.	Conductance × 10^8	Equivalent conductance.
Sept. 14	11·645	120·00	11·161	32,970	440·3
,,	,,	157·6	10·592	34,150	480·3
,,	,,	217·9	9·818	25,220	533·9
,,	,,	18·00	11·627	23,720	304·5
Sept. 15	11·945	18·00	11·927	24,140	301·9
,,	,,	100·30	11·447	33,730	439·2
,,	,,	157·9	10·865	35,060	480·7
,,	,,	218·0	10·070	36,140	534·1
,,	,,	158·4	10·860	35,220	483·1
,,	,,	100·30	11·447	33,750	439·5
,,	,,	18·00	11·927	24,230	303·1
Sept. 16	11·945	18·00	11·927	24,240	303·8
,,	,,	100·20	11·447	33,760	440·6
,,	,,	18·00	11·927	24,240	303·8
Sept. 16	11·901	18·00	11·886	24,180	303·6
,,	,,	100·11	11·408	33,650	439·6
,,	,,	158·0	10·830	34,940	480·6
,,	,,	217·6	10·039	36,140	535·7
,,	,,	18·00	11·886	24,180	303·5
Sept. 9	2·050	18·00	2·047	4,864	354·5
,,	,,	217·8	1·7287	6,569	565·6
,,	,,	18·00	2·047	4,866	354·6
Sept. 10	2·050	18·00	2·047	4,864	354·5
,,	,,	217·8	1·7287	6,542	563·3
,,	,,	18·00	2·047	4,866	354·6
Sept. 11	0·5052	18·00	0·5046	1,265·4	374·1
,,	,,	100·06	04844	2,317	713·0
,,	,,	156·4	0·4600	2,022	654·6
,,	,,	217·5	0·4262	1,683·3	587·8

Table I.—*Continued.*

Date (1905).	Concentration at 4°.	Temperature t°	Concentration at t°.	Conductance × 10⁶	Equivalent conductance.
Sept. 11	0·5052	18·00	0·5046	1,265·4	374·1
Sept. 12	0·5670	18·00	0·5663	1,409·4	371·5
"	"	99·80	0·5436	2,552	699·9
"	"	156·3	0·5165	2,222	640·7
"	"	217·4	0·4785	1,877·6	584·0
"	"	156·5	0·5165	2,228	642·4
"	"	99·81	0·5436	2,560	702·0
"	"	18 00	0·5663	1,409·9	371·6
Sept. 13	0·5238	18·00	0·5232	1,307·5	372·9
"	"	99·82	0·5022	2,392	709·9
"	"	156·5	0·4772	2,086	651·1
"	"	217·1	0·4419	1,749·2	589·0
"	"	18·00	0·5232	1,309·9	373·6
Aug. 25	1·9924	156·3	1·8149	6.590	541·4
"	"	217·5	1·6809	6,337	561·7
Aug. 26	2·032	156·5	1·8200	6,758	543·6
"	"	217·5	1·7148	6,535	567·7
Aug. 31	2·047	18·00	2·044	4,838	352·9
"	"	99·82	1·9630	7,545	573·0
Sept. 1	2·107	18·00	2·104	4,992	353·9
"	"	100·14	2·020	7,751	572·1
"	"	156·0	1·9195	6,954	539·6
"	"	217·3	1·7778	6,710	561·9
"	"	18·00	2·104	5,009	355·1
Sept. 6	2·091	18·00	2·089	4,965	354·6
"	"	217·2	1·7642	6,667	562·5
"	"	156·0	1·9051	6,932	541·9
"	"	18·00	2·089	4,960	354·8
Sept. 7	2·075	18 00	2·072	4,868	350·5

Table 1.—*Continued.*

Date (1905).	Concentration at 4°.	Temperature t°	Concentration at t°.	Conductance × 10^6	Equivalent conductance.
Sept. 7.	2·075	99·95	1·9894	7,651	573·4
,,	,,	156·2	1·8902	6,904	544·0
,,	,,	217·7	1·7499	6,766	575·5
,,	,,	156·4	1·8902	6,920	545·2
,,	,,	100·05	1·9891	7,675	575·2
,,	,,	18·00	2·072	4,926	354·7

Conductance at Round Temperatures.

The values of separate conductance, given in table 1, have been corrected to round temperature by means of temperature coefficients obtained by plotting the values: the correction did not exceed 0·2%, excep at 218°. In the following table, the column headed "Initial" gives the equivalent conductance at the temperature in question before going to higher temperature, and the column headed "Final" gives the equivalent conductance after returning to the temperature from a higher one. The agreement between initial and final values means that contamination at higher temperature was very small, and the disagreement indicates the contrary. Whenever the difference between both values at 18° exceeded 0·25 per cent., the value of the conductance were corrected by decreasing the value of the conductance at the higher temperature by two-thirds of the percentage change observed at 18°, and at the next lower temperature by one-fourth of that percentage. The values thus corrected have been indicated by affixing the letter *c*.

Table 2.—Equivalent Conductance of Sulphuric Acid.

Date (1905).	Concentration at 4°.	18°		100°		156°		218°
		Initial.	Final.	Initial.	Final.	Initial.	Final.	
Sept. 11	0·5052	374·1	374·1	713·0	—	655·4	—	588·0
Sept. 12	0·5670	371·5	371·6	700·0	702·1	641·3	643·4	584·2
Sept. 13	0·5238	372·9	373·6	710·0	—	652·1	—	589·3
Mean	0·5320	372·8	373·1	707·7	—	649·6	—	587·2
Aug. 25	1·992	—	—	—	—	541·5	—	562·1
Aug. 26	2·032	—	—	—	—	543·7	—	568·2
Aug. 31	2·047	352·9	—	573·0	—	—	—	—
Sept. 1	2·107	353·9	355·1	572·1	—	539·6	—	561·0*c*
Sept. 6	2·091	354·6	354·3	—	—	—	541·9	563·1
Sept. 7	2·075	351·5	354·7	573·3	575·2	544·1	545·3	571·1*c*
Sept. 9	2·050	354·5	354·6	—	—	—	—	565·7
Sept. 10	2·050	354·5	354·6	—	—	—	—	563·4
Mean	2·070	353·5	—	—	—	—	—	—
	2·076	—	—	572·8	—	—	—	—
	2·052	—	—	—	—	542·2	—	—
	2·057	—	—	—	—	—	—	564·9
Aug. 23	11·748	301·2	304·5	—	—	480·0	—	534·6*c*
Aug. 24	11·762	302·8	305·4	437·2	—	477·3	—	530·8*c*
Sept. 14	11·643	304·5	304·5	440·2	—	478·8	—	534·0
Sept. 15	11·945	301·9	303·1	439·1	439·3	478·9	480·8	532·7*c*
Sept. 16	11·945	303·8	303·8	440·5	—	—	—	—
Sept. 16	11·901	303·6	303·5	439·5	—	478·7	—	535·1
Mean	11·824	302·9	304·2	—	—	—	—	—
	11·839	—	—	439·3	—	—	—	—
	11·820	—	—	—	—	478·7	—	533·5

Final values of the Equivalent Conductance at Round Concentrations.

The values given in table 2 have been corrected to round concentrations, using coefficients derived from curves obtained by

plotting their functions: the error introduced into the reduction probably does not exceed 0·1 or 0·2 per cent. except those values inclosed within parenthesis. The value of conductance of sulphuric acid does not reach to a constant in ordinary dilution, as it does with a stronger acid: therefore the values of equivalent conductance at infinite dilution at 18°, 100°, 158°, and 218° were calculated by the help of the equation,

$$\Lambda_{0H_2SO_4}=\Lambda_{0K_2SO_4}+\Lambda_{0HCl}-\Lambda_{0KCl}.$$

For $\Lambda_{0K_2SO_4}$ -values, those of Noyes and Melcher[1] were used; for Λ_{0HCl} those of Noyes and Cooper;[2] and for Λ_{0KCl} those of Noyes and Coolidge.[3]

They were as follows:—

	18°	100°	156°	218°
K_2SO_4	132·8	455	715	1,065
HCl	379	850	1,085	1,265
KCl	130·1	414	625	825

Noyes and Eastman later measured the conductance, diluting my stock solution but employing a different bomb of later device: it has a special arrangement for rotating it in the heating bath, instead of doing so from outside by hand. Table 3 shows their values in comparison with mine:—

Table 3.

Comparison of Noyes and Eastman's values with mine.

Concentration.	18°		100°		155°	
	N. & E.	Kato.	N. & E.	Kato.	N. & E.	Kato.
0·5	371·8	373·2	706·3	709·0	644	645
2·0	353·7	354·1	569·8	572·2	535	536
12·5	301·7	301·0	435·0	434·8	475·3	475·4

[1] The Electrical Conductivity, 103.
[2] Ibid. 137.
[3] Ibid. 47.

In table 4, the mean values of theirs and mine are given:—

Table 4.

Final values of the equivalent conductance of sulphuric acid.

Concentration.	18°	100°	156°	218°
0·0	383	891	1,176	1,505
0·5	372·5	707·7	644·5	586
2·0	353·9	571·0	536	563
10·0	(309)	(446)	(481)	533
12·5	301.3	434·9	475	529
50	253·5	384·3	448	(502)
80	(240)	(373)	(440)	(488)
100	233·3	368·8	435	(483)

The values given in table 4 below the line of demarcation, are those of Noyes and Eastman, obtained as already mentioned.

The following table contains a comparison of the results at 18°, of previous investigations and those given in table 4:—

Comparison with previous values.

Concentration.	Kohlrausch.[1]	Whetham.[2]	Value in Table 4.
0·5	(368)	(376)	373·2
2·0	351	(350)	354·1

To the previous values, the water correction has been applied; but this has not been done in the latter case: yet the correction amounted to only 0·2 per cent. of the equivalent conductance of 0·5 milliequivalent solution. The values inclosed within parenthesis are those interpolated.

[1] Kohlrausch u. Holborn, Leitvermögen d. Elektrolyte, 160.

[2] Zeitschr. f. physik. Chem., 55, 205 (1906).

Ionization of Sulphuric Acid.

The ionization of sulphuric acid may be represented in two ways, thus :—

$$H_2SO_4 = H^+ + HSO_4^- \qquad (A)$$
$$H_2SO_4 = 2H^+ + SO_4^{--} \qquad (B)$$

There is, therefore, some explanation needed for the calculation of the degree of ionization of the acid. Denoting the concentration of the solution by C, and those of HSO_4^-, SO_4^{--}, and H^+ ions in the solution in question, by C_{HSO_4}, C_{SO_4}, and C_H respectively, we get the following equations :—

$$\Lambda = \Lambda_{0H}\frac{C_H}{C} + \Lambda_{0HSO_4}\frac{C_{HSO_4}}{C} + 2\Lambda_{0SO_4}\frac{C_{SO_4}}{C}, \qquad (1)$$

and $\quad C_H = C_{HSO_4} + 2C_{SO_4}, \quad C_{HSO_4} = C_H - 2C_{SO_4}$

$$\text{or} \quad C_{SO_4} = \tfrac{1}{2}(C_H - C_{HSO_4}) \qquad (2)$$

where Λ represents the equivalent conductance at the concentration C, and Λ_0 that at the infinite dilution.

From (1) and (2), we get for the concentration of H^+ ion, the following,

$$\left.\begin{aligned} \frac{C_H}{C} &= \frac{\Lambda}{\Lambda_{0H} + \Lambda_{0HSO_4}} - \frac{C_{HSO_4}}{C}\,\frac{\Lambda_{0HSO_4} - \Lambda_{0SO_4}}{\Lambda_{0H} + \Lambda_{0SO_4}} \\ \frac{C_H}{C} &= \frac{\Lambda}{\Lambda_{0H} + \Lambda_{0HSO_4}} - \frac{C_{SO_4}}{C}\,\frac{\Lambda_{0SO_4} - \Lambda_{0HSO_4}}{\Lambda_{0H} + \Lambda_{0HSO_4}} \end{aligned}\right\} \qquad (3)$$

Representing the concentration of H^+ ion by C'_H, when the ionization takes place wholly as (A), and by C_H'', when it takes place wholly as (B), we get the equations

$$\Lambda = \frac{C_H}{C}\Lambda_{0H} + \frac{C_{HSO_4}}{C}\Lambda_{0HSO_4},$$

and $$\Lambda = \frac{C''_H}{C}\Lambda_{0H} + \frac{2C_{SO_4}}{C}\Lambda_{0HSO_4}$$

As $C'_H = C_{HSO_4}$ and $C''_H = 2C_{SO_4}$, these two equations may be transformed, thus

$$\left.\begin{aligned} &\Lambda = C'_H(\Lambda_{0H} + \Lambda_{0HSO_4})/C \\ \text{and}\quad &\Lambda = C''_H(\Lambda_{0H} + \Lambda_{0SO_4})/C \end{aligned}\right\} \quad (4)$$

$$\left.\begin{aligned} \text{or}\quad &\frac{C'_H}{C} = \frac{\Lambda}{\Lambda_{0H} + \Lambda_{0HSO_4}} \\ \text{and}\quad &\frac{C''_H}{C} = \frac{\Lambda}{\Lambda_{0H} + \Lambda_{0SO_4}} \end{aligned}\right\} \quad (5)$$

By eliminating Λ, Λ_{0SO_4} and Λ_{0HSO_4} between (3) and (4), the following equations were obtained :—

$$\left.\begin{aligned} &\frac{C_H}{C} = \frac{C''_H}{C} - \frac{C_{HSO_4}}{C}\,\frac{C''_H - C'_H}{C'_H} \\ \text{and}\quad &\frac{C_H}{C} = \frac{C'_H}{C} + \frac{2\,C_{SO_4}}{C}\,\frac{C''_H - C'_H}{C''_H} \end{aligned}\right\} \quad (6)$$

By the help of these equations, the actual concentration of the H^+ ion and the concentration of one of SO_4^{--} and HSO_4^- ion can be calculated, when C'_H, C''_H, and either one of C_{HSO_4} or C_{SO_4} are known. If difference $C''_H - C'_H$, is small compared with C'_H and C''_H, the calculation of concentration of H^+ ion will be fairly accurate.

There is a relation expressed by

$$C = C_{H_2SO_4} + C_{HSO_4} + C_{SO_4}$$

By eliminating C_{HSO_4} or C_{SO_4} between this equation and (2), we obtain

$$\left.\begin{aligned} &\frac{C_{SO_4}}{C} = \frac{C_{H_2SO_4}}{C} + \frac{C_H}{C} - 1 \\ \text{or}\quad &\frac{C_{HSO_4}}{C} = \frac{2\,C_{H_2SO_4}}{C} + \frac{C_H}{C} - 2 \end{aligned}\right\} \quad (7)$$

These show that, if actual concentration of the H^+ ion and that of the undissociated portion were known, the concentration of SO_4^{--} aud HSO_4^- ions may be calculated.

Limiting Values of Concentrations of Hydrogen-ion.

The ratio of concentration of H^+ ion ionized as (A) and (B) to the total concentration of sulphuric acid, can be calculated by the help of equation (5), if the values of $\Lambda_{oH}+\Lambda_{oSO_4}$ and $\Lambda_{oH}+\Lambda_{oHSO_4}$ are known. Now, the former values are those of equivalent conductance of sulphuric acid at infinite dilution, and are given in table 4. But the values of $\Lambda_{oH}+\Lambda_{oHSO_4}$ have not yet been found, so far as I know. Yet at 18° it will possibly not be far from the value of Λ_o of acetic acid. Moreover, the equivalent conductance of di-ionic electrolytes approach each other at higher temperatures.[1] Therefore Noyes and Cooper's values of acetic acid were used for those of $\Lambda_{oH}+\Lambda_{oHSO_4}$. They are as follows:—

18°	100°	156°	218°
347	773	980	1·168

The values of the concentration of the hydrogen ion, calculated by the help of equation (5), using for the values of $\Lambda_{oH}+\Lambda_{oSO_4}$ and $\Lambda_{oH}+\Lambda_{oHSO_4}$ those mentioned above, are given in table 5. In the table, the first of two values separated by a dash is 100 times the former value; the second one 100 times the latter value. It will be clear that these two values represent the limits between which must lie the percentage concentration of the hydrogen ion actually existing in the solution.

[1] The Electrical Conductivity, 336.

Table 5.

Percentage ionization of sulphuric acid: approximate values.

Concentration.	18°	100°	156°	218°
0·0	100·0	100·0	100·0	100·0
0·5	98–108	80–92	55–66	39–50
2·0	92–102	64–74	46–55	37–48
10·0	81–89	50–58	41–49	35–46
12·5	79–87	49–56	40–48	35–45

From the table, it will be seen that the two values are not very different.

Final Values of the Degree of Ionization.

It is evident that, if sulphuric acid ionizes wholly into $2H^{+}+SO_4^{--}$, the percentage values of the degree of ionization will be the first values of table 5; and if wholly into $H^{+}+HSO_4^{-}$, the percentage values will be twice the second ones. Now, a comparison of the latter values with the percentage values of the degree of ionization of hydrochloric acid is given below:—

Concentration.		100°	156°	218°
6·25	HCl	97	93	91
6·25	$H.HSO_4$	112	96	90

The values for hydrochloric acid were obtained by interpolation between Noyes and Cooper's values. From the comparison, the agreement between the degree of ionization of both acids, at high temperature, is remarkable. It will be interesting to note the comparison given by Noyes and Eastman at higher concentration; and therefore it is inserted here:—

Concentration.		100°	156°	218°
40	HCl	92	90	86
40	$H.HSO_4$	96	90	84

This shows that the agreement at higher concentration persists at lower temperature. The disagreement at lower temperature and lower concentration, may be accounted for by the accompaniment of ionization into SO_4^{--} ion. That the second ionization does not take place to any appreciable extent, is also to be seen from the ionization of potassium hydrogen sulphate calculated by Noyes and Eastman, therefore it is given here:—

Concentration.	100°	156°
10	18–27	0–10
50	4–13	0–3
100	1–10	0–2

The values separated by a dash show the limits between which must lie the percentage ratio of hydrogen-ion concentration to total acidic hydrogen concentration of a solution of the salt. The second ionization of sulphuric acid must be smaller than the ionization of potassium hydrogen sulphate producing hydrogen-ion, because in the former case hydrogen-ion from the first ionization depresses the second ionization. Now, it becomes clear that hydrochloric acid and $H.HSO_4$ have, at higher temperature and higher concentration, nearly the same ionization tendency. In the following calculation, it is assumed that the degree of ionization of sulphuric acid into $H^+ + HSO_4^-$ is equal to that of hydrochloric acid, and also that SO_4^{--} -ion is produced by further ionization of a part of the HSO_4^- thus ionized.

By the help of this reasonable assumption, the undissociated portion may be calculated by the values of the degree of ionization of hydrochloric acid determined by Noyes and Cooper, as given here:—

Concentration.	18°	100°	156°	218°
1	99	98	97	97
5	98	96	95	94

Now, from the concentration of the undissociated portion, the concentration of SO_4^{--} and HSO_4^- ions can be calculated by the

equation (7), if C_H is known. Preliminary values of C_{SO_4} and C_{HSO_4} were calculated, using twice the mean of pairs of values given in table 5 as the values of C_H/C. Then, more correct values of concentration of H^+ ion were calculated by means of equation (6), using those values. The mean of the pair of values of concentration of hydrogen ion, obtained thereby, was taken as the final value of concentration of hydrogen ion. The final values of C_{SO_4} and C_{HSO_4} were calculated therefrom by equation (7). The results are given in table 6:—

Table 6.—The Ionization-relations of Sulphuric Acid.

Temperature.	Concentration.	$\frac{100C_H}{C}$	$\frac{100C_{H_2SO_4}}{C}$	$\frac{100C_{HSO_4}}{C}$	$\frac{100C_{SO_4}}{C}$	$\frac{10^6 C_H C_{SO_4}}{C_{HSO_4}}$
18°	1	185	1	13	86	12,200
	5	164	2	32	66	17,000
100°	1	136	2	60	38	860
	5	112	4	80	16	1,100
156°	1	108	3	88	10	130
	5	97	5	93	2	93
218°	1	97	3	97	0	—
	5	93	6	94	−1	—

The value of ionization-constant at a temperature given in the table is not very constant.[1]

The result of calculation at 18° was checked, as at that temperature there were several previous data available for the purpose. By the help of Nernst's work,[2] the heat of ionization of HSO_4^- ion into $H^+ + SO_4^{--}$ was calculated in two ways and compared. First, van't Hoff's well known equation,

$$\frac{d \log k}{dT} = \frac{q}{RT^2},$$

[1] Recently, Luther calculated the constant, using a little different assumption, and obtained a not very constant value (Zeitschr. f. Elektrochem. **13**. 294 (1907)).

[2] Theor. Chemistry 658, (1904).

was integrated between K_1, T_1, and K_2, T_2, by the assumption that the internal energy-change attending the ionization was a linear function of temperature expressed by the equation,

$$q = q_0 + aRT, \tag{8}$$

and the following equation was obtained,

$$\log\frac{K_2}{K_1} = \frac{q_0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + a\log\frac{T_2}{T_1} \tag{9}$$

An application of this formula to the calculation of the heat of ionization of a substance, whose ionization-constant is very changeable, can hardly give an accurate result. But, provided the value of K at two temperatures be taken at the same concentration, it will probably give a rough approximation. Substituting in equation (9) $K_1 = 17{,}000$, $T_1 = 291$; and $K_2 = 1{,}100$, $T_2 = 373$, one equation was obtained; and substituting in the equation $K_1 = 860$, $T_1 = 373$; $K_2 = 130$, $T_2 = 429$, another was obtained. From the simultaneous equations, values of a and q_0 were obtained. Substituting these two values in equation ( ), −4710 calories were obtained for the value of the heat of ionization, here a negative value meaning the evolution of heat. Noyes and Eastman calculated the heat of ionization from Thomsen's value, applying their own ionization data, and obtained 5020 cal. This is a fairly close agreement, so far as the nature of the data is concerned.

Summary and Conclusion.

In the present investigation, a special cell (a bomb) was employed for measuring the conductivity of sulphuric acid at 18° 100°, 156°, and 218°; the result has been given in table 4. In calculating the degree of ionization, the equivalent conductivity of $H^+ + HSO_4^-$, when completely ionized, was assumed to be equal to that of acetic acid at infinite dilution. It was assumed also that the degree of ionization of the acid into $H^+ +$

HSO_4^- was equal to that of hydrochloric acid. The result has been given in table 6. The result was checked by the help of van't Hoff's equation and thermochemical data.

In conclusion, hearty thanks are due to Professor Noyes, under whose kind guidance this investigation was prosecuted.

On the Reaction between Ferric Chloride and Potassium Ferricyanide.

By

Yogoro Kato.

In ordinary text-books on analytical chemistry, nothing more is said about the reaction between ferric chloride (and other ferric salts) and potassium ferricyanide in solution, than that these two salts give a brownish-red colouration. Talbot, however, in his "Quantitative Chemical Analysis," states that potassium ferricyanide, when used as an outside indicator for the end-point of the titration of ferrous salt against a bichromate solution, gives a blue colouration with ferric salt, after standing a long time, on account of the reduction of ferric salt by the presence of dust under the action of light.

Spring[1] carried on investigations connected with the reaction now under consideration, and found that, in an aqueous solution of ferric chloride (126 : 100), the ferricyanide caused a precipitation of Prussian blue accompanied by an evolution of chlorine; but that, in a more concentrated solution—say 230 : 100,—it produced no such change. He attributed the reaction to the possible change in the facility of decomposition of ferric chloride due to the change in the concentration of its solution. The reaction between the two named salts has an important bearing upon the analysis, but such reaction, as is mentioned above, can take place only in a very concentrated solution, such as is very seldom used in practice, so that it might not be necessary to investigate further, provided there were no phenomenon besides that observed by Spring. Nevertheless, as will be seen later,

[1] Bl. Ac. r. Belg. (3), **24**, 255 : Ref. Chem. Centralbl., **2**, 998 (1892).

in the presence of a large quantity of another salt, these two salts react even in a dilute solution, producing a blue colouration. Hence, the author feels that it will be interesting and useful to prosecute research upon the subject.

Action of Patassium Ferricyanide upon Ferric Chloride in its Concentrated Solutions.

Wiih the purpose of repeating partly the reactions observed by Spring, a drop of a one-molar solution of potassium ferricyanide was added to 5 c. c. of each one of several solutions of ferric chloride having different concentration; and the result was as follows:—

> A blue colouration appeared within one minute, after the addition of the ferricyanide, in a 6–0·7 molar-solution of ferric chloride; but it took more than ten minutes for the colouration to appear in solutions more dilute than 0·5 molar.

In the case when the colouration appeared quickly, an evolution of chlorine was generally observed; as Spring had noted.

Action of Ferric Chloride upon Potassium Ferricyanide in its Concentrated Solutions.

To see if the reaction would take place in concentrated solutions of either of the two salts, one drop of a one-molar solution of ferric chloride was added to solutions of potassium ferricyanide of different concentration, but no colouration was observed. This shows that the reaction under consideration takes place in a concentrated solution of ferric chloride, but not in one of potassium ferricyanide.

Explanation of the Reaction.

It seems plausible to explain the reaction between the two salts above-mentioned, upon one or more of the following assumptions:—

I. The reaction takes place because of the elimination of ferrous salt from the system of the equation,

$$2FeCl_3 \rightleftarrows 2FeCl_2 + Cl_2 \qquad (1)$$

II. The reaction occurs as the result of the elimination of chlorine from equation (1).

III. By increasing the concentration of ferric chloride, that of ferrous salt rises according to equation (1); so that the precipitation of Prussian blue[1] may take place.

IV. By changing the concentration of the solution of ferric chloride the ions $FeCl_2^{\cdot}$ and Cl' are discharged, ferrous chloride and chlorine being formed thereby, and the reaction under consideration results.

V. The reaction proceeds by the elimination of a ferrocyanide from the system of the equation,

$$2K_3Fe(CN)_6 + 2MCl \rightleftarrows 2MK_3Fe(CN)_6 + Cl_2 \qquad (2)$$

VI. The reaction proceeds as a result of the elimination of chlorine from the system of equation (2).

VII. The reaction takes place as a result of the increase in quantity of a chloride (MCl) in the system of equation (2).

VIII. By increasing the concentration of potassium ferricyanide, the precipitation of ferrous ferricyanide becomes possible; or in equation (2) the concentration of ferrocyanide becomes sufficient to cause the precipitation of Prussian blue.

IX. The presence of dust in the reagents or water used in preparing the solution causes the reduction of the two salts, and the reaction under consideration results.

It is the aim of the present investigation to determine (if possible) which assumption is the most probable one; and in the following discussion, each will be considered separately.

[1] Here and also in the succeeding parts, Prussian blue and Turnbull's blue are regarded as identical. Compare Hofmann and others' papers (Lieb. Ann., 337, 1, 1905.)

I. The reaction takes place because of the elimination of ferrous salt from the system of the equation,

$$2FeCl_3 \rightleftarrows 2FeCl_2 + Cl_2 \qquad (1)$$

If the ferrous salt is removed from the system of the equation, the reaction will take place in the right direction. Now, the reaction between ferrous chloride and potassium ferricyanide may bc represented thus :—

$$3FeCl_2 + 2K_3Fe(CN)_6 = Fe_3Fe_2(CN)_{12} + 6KCl$$

The removal, by this equation, of ferrous ferricyanide removes ferrous chloride from equation (1). It looks quite probable that ferric chloride has the power to remove $Fe_3Fe_2(CN)_{12}$ by precipitating it; because it is well known that Prussian blue forms a colloidal solution, and also that a salt, giving an ion of high valency, has the power to precipitate a colloid having an opposite electric charge.

By passing an electric current through water containing Prussian blue colloid, it was quickly seen that precipitation took place around the anode; which shows that Prussian blue forms an electrically negative colloid. Now, it is interesting to determine if the reaction under consideration will take place in a solution which behaves like ferric chloride with respect to precipitation of a colloid. With this in view, some experiments were conducted.

The reaction between ferric chloride and potassium ferricyanide in a solution of aluminium salts.

A. The reaction in a solution of aluminium chloride.

At first, aluminium chloride was selected, as it is very similar to ferric chloride in its chemical behaviour. To each portion of several of 5 c. c. of its solution at different concentrations, a drop of a 1-molar solution of ferric chloride and the same quanity o a 1-molar solution of potassium ferricyanide were added and the mixture shaken. The range of concentration of the aluminium

chloride solution, in which the blue colouration took place, was carefully studied, with the following results:—

> The colouration took place within one minute in 3·2–0·8–molar solution, while it required more than ten minutes in the solution when more dilute than 0·6–molar.

From this it is seen that, not only in the concentrated solution of ferric chloride, but in that of aluminum chloride, the reaction under consideration takes place. It is also seen that the range of concentration of both solutions in which the reaction takes place is very like.

B. The reaction in a solution of aluminium sulphate.

The experiments with aluminium chloride which have just been described, induced the undertaking of a further one with aluminium sulphate, which might behave differently from the chloride. Experiments, quite similar to the preceding, were made with solutions of aluminium sulphate of different concentrations. The results were as follows:—

> Instantaneously a blue colouration was observed in the 2–0·7–molar solution (taking ½ $Al_2(SO_4)_3$ as 1 mol.); but it required more than ten minutes in a solution diluter than 0·5 molar.

This experiment, taken in connection with the previous one, shows that these aluminium salts act in a very similar way in causing the reaction under consideration.

The reaction between ferric chloride and potassium ferricyanide in solutions of salts of tetravalent metals.

Inasmuch as it looks, from the previous experiments, as if the reaction takes place as a result of the precipitation of Prussian blue in the presence of salts of trivalent metals, it will be interesting to study the relation of salts of tetravalent metals to the reaction under consideration. For this purpose, platinum chloride and stannic chloride were taken, and with them the following results were obtained:—

A. Platinum chloride showed the reaction in its 1·5-molar solution within one minute; while in its 0·3 molar solution, it required more than ten minutes.

B. Stannic chloride showed the reaction in its 1·5-molar solution within one minute; while in its 0·4-molar solution, it required one hour.

The stannic chloride used in the experiments may have contained stannous chloride, which reduced ferric salt or ferricyanide, and thus caused the reaction. So it was tested with mercuric chloride for stannous salt, but there was no indication of its presence. Again, the stannic chloride solution was boiled with the addition of ferric chloride, and then experiments similar to (B) were performed, but there was no difference whatever in the results. This shows that only a trace, if any, of stannous salts was present; and was not sufficient to give the reaction under consideration. The above experiments convince us that the reaction very likely occurs because of the precipitation of the colloid by the salts of tetravalent metals.

The reaction between ferric chloride and potassium ferricanide in the solutions of the salts of divalent metals.

After knowing the relation of the salts of trivalent and tetravalent metals to the reaction, it becomes interesting to extend the experiments to the reaction of salts of divalent metals, which are known also to have the capacity of precipitating, to a great extent, a colloid. Therefore, experiments with some common salts of this kind were undertaken, and the results were as follows:—

A. Magnesium chloride gave, in its 3-molar solution, a blue colouration within one minute; but in its solution more dilute than 2-molar, it took more than ten minutes.

B. Magnesium sulphate gave, in its 2–1·2 molar solution, a blue colouration within one minute; but in its solution more dilute than 1-molar, it took more than ten minutes.

C. Calcium chloride gave, in its 1·5–0·8 molar solution, a blue colouration within one minute; but in its solution more dilute than 0·5 molar, it took more than ten minutes.

In all concentrated solutions of the magnesium and calcium salts, as with the salts of higher valency, an intense blue colouration was observed, accompanied by an evolution of chlorine. In the solutions of salts of divalent metals, as shown hereinbefore, the range of concentration in which the colouration was observed, is very similar.

The reaction between ferric chloride and potassium ferricyanide in the solutions of salts of monovalent metals.

The results of the experiments with solutions of salts of metals possessing higher valency, induced further research with salts of monovalent metals which, as is well known, have capacity of precipitating a colloid in only a slight degree. Therefore, experiments with some of these salts were undertaken, and the results were as follows:—

A. Sodium chloride induced a blue colouration in its 6-molar solution within one minute; but in its 3-molar it took more than ten minutes.

B. Potassinm chloride took more than ten minutes for the blue colouration to appear in its 3-molar solution.

C. Lithium chloride acted in a way similar to that of sodium chloride.

The reaction between ferric chloride and potassium ferricyanide occurs as was expected, only in very concentrated solutions of these salts.

Summary of the experiments to show the relation between the concentration of the solutions of salts of metals of different valency and their behaviour toward the reaction between ferric chloride and potassium ferricyanide.

For convenience of a general survey of the relation, the results of the experiments performed are summarized in the following table :—[1]

Salts. \ Concentration.	6	3	2	1·5	1·2	1·0	0·8	0·7	0·6	0·5	0·4
$FeCl_3$	o	o	o	o	o	o	o	o		+	
$AlCl_3$		o	o	o	o	o	o		+		
$\frac{1}{2}Al_2(SO_4)_3$...			o	o	o	o	o	o			+
$MgCl_2$		o	+								
$MgSO_4$		o	o	o	o	+					
$CaCl_2$				o	o	o	o			+	
KCl.....		+									
NaCl	o	+									
LiCl	o	+									
$PtCl_4$			o								
$SnCl_4$			o								

The concentration of the salts is expressed in the above table in number of gramme-molecules in one litre of the solution. In the experiments, one drop each of 1–molar solution of ferric chloride and of potassium ferricyanide were added to 5 c. c. of the solution of the salts. The reagents used were pure ones of Merck's preparation, and to their concentrated solutions ferric chloride and potassium ferricyanide were added separately, to see whether either of the salts caused a colouration in the solution or not: but no such change was observed.

Upon inspecting the table, it will be noticed that the salts of metals having the same valency have, in their solutions of equal concentration, nearly equal capacity for promoting the reaction. This reaction takes place in a more dilute solution in the case

[1] The "o" in the table is to show that the reaction took place within one minute, and "+" that it required ten minutes.

of the salts of metals of higher valency. This phenomenon reminds us of the precipitation of a colloid by an electrolyte.

The precipitation of colloidal Prussian blue by salts.

A colloidal solution of Prussian blue was prepared by adding 1 c. c. each of 0·01- equivalent solutions of ferrous ammonium sulphate and potassium ferricyanide to 20 c. c. of water. The solution thus prepared was blue and perfectly transparent. To this solution, those of different salts were added until precipitation took place: the results being as follows:—

Solutions added to 22 c.c. of the coll. sol.	$AlCl_3$ $^1/_{10}$ molar.	$MgCl_2$ $^1/_{10}$ molar.	NaCl $^1/_{10}$ molar.
5 c.c.	o	o	o
3	o	o	+
2·5	o	?	
2	?	+	
1	+		

Here the sign "o" shows that the precipitation took place in a short time, and "+" shows that it did not occur within ten minutes. The relation, shown in the table between the precipitation and the valency, will be found to be closely connected with that, given in the previous table, between the concentration of salts, in which the reaction under consideration occurs, and the valency. This seems to show that there is close relation between the said reaction in the solutions of different salts and the precipitation of the colloid by the salts. Now, it looks quite probable that the reaction under consideration will take place in a solution having the power to precipitate the colloid to a certain extent.

II. The reaction follows as the result of removal of chlorine from the equation,

$$2FeCl_3 \rightleftarrows 2FeCl_2 + Cl_2$$

The removal of chlorine from the system represented by the equation, may produce ferrous chloride in sufficient quantity for the reaction to take place. The removal may be accomplished by a reduction of the solubility. So far as the author knows, the solubility of chlorine in the solution of a chloride is generally less than that in pure water.[1]

Some solubility determinations were made in the usual way and are given, together with the results of previous determinations, in the following table :—

Salts.	Results given in Seidell's.[1]			Kato.		
	Concentration.	Temperature.	Solubility coefficient.	Concentration.	Temperature.	Solubility coefficient.
—	0	10°	2·7	—	—	—
NaCl	3·3	15°	0·95	3·0	16°	0·94
$CaCl_2$	0·5	12°	0·79	2·3	17°	0·88
$AlCl_3$	—	—	—	1·0	17°	1·03

From this table it will be seen that there is a parallelism between the solubility of chlorine in the solution of the salts and the valency of their metals. This fact may be the cause of the reaction under consideration. Hence, another experiment was performed in order to study the influence of solubility.

The reaction between ferric sulphate and nitrate[2] and potassium ferricyanide.

A study of the action of ferric sulphate and nitrate, instead of chloride, upon ferricyanide, may throw some light on the reaction under consideration. In this case, oxygen instead of chlorine will be given off as the result of the reaction, if there is any, and the solubility of the former is very small when compared

See Seidell, Solubilities of Inorganic and Organic Substances, 113–114, (1907).

[2] Spring also studied the reaction between ferric nitrate and the ferricyanide.

with that of the latter. If the solubility of chlorine has much influence upon the reaction, some difference should be observed. To 5 c. c. of solutions of aluminium sulphate of different concentrations, one drop of a 3-equivalent solution of ferric nitrate and one drop of potassium ferricyanide were added, and the results were as follows:—

A blue colouration occurred in the 2–0·5 molar solution ($\frac{1}{2}Al_2(SO_4)_3$ being taken as one molecule) within one minute, while in the more dilute solutions it appeared only after a long time. In this case, the intensity of the colouration was somewhat less than in the reaction of ferric chloride. Again, to a concentrated solution of ferric nitrate, one drop of potassium ferricyanide was added; and an intensely blue colouration occurred. Now, the concentration of the salt-solutions, in which the reactions under consideration took place, was not greatly influenced by the difference of anion, so far as this experiment went. It seems to be quite probable that there is another reason for the reaction than the solubility of chlorine.

III. By increasing the concentration of ferric chloride, that of ferrous salt may rise according to the equation,

$$2FeCl_3 \rightleftarrows 2FeCl_2 + Cl_2,$$

so that a precipitation of Prussian blue may occur.

That this assumed reaction does not play an important part is readily seen from the experiments which have been discussed: they show that the reaction takes place in a dilute solution of ferric chloride when another salt is present.

IV. By changing the concentration of ferric chloride, the discharge of the ions, $FeCl_2^{\cdot}$ and Cl', may take place more easily, and ferrous chloride and chlorine may be formed.

Spring[1] electrolyzed ferric chloride with an iron anode and a

[1] Loc. cit.

platinum cathode, and found that the passing of the current was easier in a certain given solution than in another having a different concentration. He also dissolved iron in a solution of ferric chloride, and found that the dissolving of the metal is easier in a certain given solution than in another having a different concentration. He then discovered that there is a parallelism, between the promptness of the dissolving and the reaction under consideration, with regard to the concentration of a solution of ferric chloride; i. e., the reaction takes place more readily in that solution in which the metal dissolves more easily. According to this, there must be some connection between the reaction and the decomposition electromotive force of ferric chloride; i. e., the reaction under consideration must take place in the solution which has the least value for the decomposition electromotive force.

Some measuremeuts of the decomposition electromotive force were therefore prosecuted with the method given by Ostwald and Luther.[1] The cell employed was a U-shaped glass tube: the current passed through the solution was measured by a reflection galvanometer made by Hartmann and Braun, (the internal resistance being 63 ohms,) using a 7 ohms shunt. The current was obtained from a lead accumulator, compared with Weston and Clark cells, constructed by using pure chemicals prepared by Merck. The value for the decomposition electromotive force was obtained graphically from the relation between the current strength and the electromotive force measured between the platinum and calomel electrodes. The results are given in the following table:—

[1] Ostwald und Luther, Phys.-chem. Messungen, 391 (1902).

Concentration.	I.			II.		
	Current strength.	E. M. F. between calomel electrode & anode.	cathode.	Current strength.	E. M. F. between calomel electrode & anode.	cathode.
½ mol.	0	0·603	0·603	0	0·582	0·582
	1	0·878	0·577	2	0·770	0·562
	1	0·993	0·563	2	0·978	0·562
	3	1·049	0·539	8	1·061	0·541
	20	1·085	0·478	60	1·098	0·478
	60	1·122	0·410	220	1·127	0·395
	140	1·137	0·331			
	280	1·186	0·181			
Decomposition E.M.F. at each electrode.		1·09	0·50		1·05	0·51
Decomposition E.M.F. of the solution.		0·59			0·54	

Concentration.	I.			II.		
	Current strength.	E. M. F. between calomel electrode & anode.	cathode.	Current strength.	E. M. F. between calomel electrode & anode.	cathode.
1-mol.	0	0·609	0·612	0	0·603	0·613
	1	0·892	0·583	0	0·804	0·603
	1	0·989	0·583	0	0·994	0·583
	5	1·049	0·543	6	1·047	0·543
	32	1·085	0·476	42	1·075	0·470
	82	1·116	0·410	100	1·106	0·394
	160	1·146	0·342	180	1·106	0·322
	320	1·194	0·197		1·166	0·161
Decomposition E.M.F. at each electrode.		1·09	0·51		1·06	0·50
Doçomposition E.M.F. of the solution.		0·58			0·56	

Concentration.	I.			II.		
	Current strength.	E. M. F. between calomel electrode & anode.	cathode.	Current strength.	E. M. F. between calomel electrode & anode.	cathode.
2–mol.	0	0·623	0·623	0	0·623	0·623
	1	0·905	0·593	0	1·005	0·589
	1	0·997	0·583	50	1·075	0·466
	8	1·069	0·543	480	1·105	0·390
	43	1·085	0·474			
	90	1·109	0·402			
	160	1·135	0·331			
	320	1·186	0·181			
Decomposition E.M.F. at each electrode.		1·07	0·54		1·07	0·50
Decomposition E.M.F. of the solution.		0·53			0·57	

Concentration.	I.			II.		
	Current strength.	E. M. F. between calomel electrode & anode.	cathode.	Current strength.	E. M. F. between calomel electrode & anode.	cathode.
3–mol.	0	0·633	0·633	0	0·643	0·643
	1	1·005	0·591	1	1·013	0·603
	7	1·051	0·541	8	1·049	0·543
	18	1·081	0·472	20	1·085	0·470
	50	1·132	0·322		1·129	0·322
	80	1·176	0·165			
Decomposition E.M.F. at each electrode.		1·09	0·40		1·07	0·42
Decomposition E.M.F. of the solution.		0·69			0·65	

The electromotive force between the calomel electrode and anode was in the direction of the latter electrode, and that between the calomel electrode and cathode also toward the latter electrode.

The first zero value for the current strength means that no current was passed from any external source. Two similar successive values for the current strength show that the current was a little increased over the first; but the increase was not readable on the galvanometer. The values of the current strength are expressed by the scale-reading of the galvanometer.

The following table shows a summary of the above experiments :—

Concentration.	Decomposition E. M. F. of the Solutions.		
	I.	II.	Mean.
½-mol.	0·59	0·54	0·57
1-mol.	0·58	0·56	0·57
2-mol.	0·53	0·57	0·55
3-mol.	0·69	0·65	0·67

From this table, it is seen that no appreciable change due to the change of concentration of the solution is to be detected in the electromotive force. Then some trials were made to measure the decomposition electromotive force, to see the difference, an iron anode and a platinum cathode being used; but a constant voltage applied in passing the current through the solution did not give any constant reading on the galvanometer; i. e., the needle was moving backward and forward within a wide range,[1] consequently, no measurement was registered.

From the result of these experiments, it seems probable that Spring would have obtained a different result if he had used a platinum anode, instead of an iron one, in passing the current

[1] This phenomenon was observed by Fregenhangen (Zeitschr. f. physik. Chem., **43**, 1, 1903) and Heathcote (Zeitschr. f. physik. Chem., **37**, 368 1901).

through the solution. The readiness with which the current passed through the solution is changed also by the changing resistance which the solution offers; i. e., the current flows more readily through a solution having less resistance than through one having more. To get a rough idea of the comparative magnitude of the resistance of the solution, the following described experiment was performed:—

Solutions of ferric chloride of different concentrations were introduced into the U-shaped tube which had been used in measuring the decomposition electromotive force. The resistance was measured by the usual method for measuring the electric conductivity of a solution. The resistance thus measured was that which the solution offered between the electrodes at a constant distance in a room wherein the temperature was changing 2–3 degrees. The results were as follows:—

Concentration.	Resistance in ohms.
½–mol.	320
1–mol.	250
2–mol.	280
3–mol.	1200

This shows clearly that the passing of the current through the solution is largely influenced by the change in its concentration.

The decomposition electromotive force of ferric chloride may be calculated also from the electromotive force required for the changes, $Fe^{\cdot\cdot\cdot} \rightarrow Fe^{\cdot\cdot}$ and $2Cl' \rightarrow Cl_2$. The electromotive force which is produced in the change, $Fe^{\cdot\cdot\cdot} \rightarrow Fe^{\cdot\cdot}$, may be expressed, as usual, by the equation,

$$F = F_0 + \frac{RT}{Q} \ln \frac{C_{Fe^{\cdot\cdot\cdot}}}{C_{Fe^{\cdot\cdot}}},$$

where F_0 represents the electromotive force produced, when the

concentrations of the ferric and ferrous ions are one formula weight per litre, and $C_{Fe}^{\cdots}$ and $C_{Fe}^{\cdot\cdot}$ the concentrations of the ions $Fe^{\cdots}$ and $Fe^{\cdot\cdot}$ respectively. Using Maitland's value,[1] 0·46, for F_0 and usual values for Q and R, above equation may be transformed into

$$F = 0{\cdot}46 + 0{\cdot}059 \log \frac{C_{Fe}^{\cdots}}{C_{Fe}^{\cdot\cdot}}.$$

Similarly the electromotive force required for the change, $2Cl' \rightarrow Cl_2$, may be represented by using Luther and Sammet's value,[2] 1·12, for F_0, as follows:

$$F = 1{\cdot}12 + 0{\cdot}059 \log \frac{\sqrt{C_{Cl_2}}}{C_{Cl'}}$$

The electromotive force required for the change of ferric chloride into ferrous chloride and chlorine will, therefore, be the difference of two electromotive forces. Thus, the electromotive force, which might also be called a decomposition electromotive force of ferric chloride, may be expressed by the equation:

$$\pi = 1{\cdot}12 - 0{\cdot}46 + 0{\cdot}059 \log \frac{\sqrt{C_{Cl_2}}}{C_{Cl'}} - 0{\cdot}059 \log \frac{C_{Fe}^{\cdots}}{C_{Fe}^{\cdot\cdot}}$$

$$= 0{\cdot}66 + 0{\cdot}059 \log \frac{\sqrt{C_{Cl_2}} \cdot C_{Fe}^{\cdot\cdot}}{C_{Cl'} \cdot C_{Fe}^{\cdots}}.$$

Now, for the concentrated solutions, it may be assumed that ferric chloride dissociates mainly into $FeCl_2^{\cdot}$ and Cl' ions. Thus, the relations, $\gamma C_{Fe}^{\text{III}} = C_{Cl'}$ and $\beta C_{Fe}^{\text{III}} = C_{Fe}^{\cdots}$, will be kept up pretty well, where γ represents the degree of dissociation of ferric chloride into those two ions, β that into $Fe^{\cdots}$ and $3Cl'$ ions, which should be very small, and C_{Fe}^{III} the total concentration of the ferric salt. There is also a relation, $C_{Fe}^{\cdot\cdot} = 2C_{Cl_2}$. Assuming arbitrarily for simplicity that the formula, $1 - \gamma = KC^{\frac{1}{2}}_{Fe^{\text{III}}}$,[3]

[1] Zeitschr. f. Elektrochem., **12**, 263 (1906).

[2] Zeitschr. f. physik. Chem., **11**, 293 (1905).

[3] Cf. A. A. Noyes Technology Quarterly, **17**, 293; Zeitschr. f. physik. Chem., **52**, 635 (1905).

holds good even in the concentrated solutions, above equation may be transformed into,

$$\pi = 0{\cdot}66 + 0{\cdot}059 \log \frac{C^{\frac{3}{2}}_{Fe^{\cdot\cdot}}}{\sqrt{2}\,(1 - KC^{\frac{1}{2}}_{Fe^{III}})\beta C^{2}_{Fe^{III}}},$$

where the value of K will be something like 0·5 when it is assumed that the value should not be very far apart from that for a uni-univalent salt like potassium chloride.

In such a range of the concentration of ferric chloride as in the present investigation, $1 - KC^{\frac{1}{2}}_{Fe^{III}}$ and $C^{2}_{Fe^{III}}$ can not be very large and also their product. Thus, in the case when the sign of π becomes minus, that is to say, the decomposition takes place without any external force, $C^{\frac{3}{2}}_{Fe^{\cdot\cdot}} / \beta$ should be very small. When π is equal to zero, the relation will be

$$C^{\frac{3}{2}}_{Fe^{\cdot\cdot}} / \beta = 1{\cdot}4 \times 10^{-11}(1 - KC^{\frac{1}{2}}_{Fe^{III}})C^{2}_{Fe^{III}}$$

The decomposition can take place without any external force, when the left side of the equation is equal to or smaller than the right. Supposing β is small, $C_{Fe^{\cdot\cdot}}$ must be, therefore, extremely small. Now, in such a dilute solution, it may be assumed that ferrous salt is completely dissociated into the ferrous ion, so that $C_{Fe^{\cdot\cdot}}$ may represent the concentration of the ferrous salt. A trace of ferrous salt, however, is not sufficient to produce the reaction under consideration. It is evident, therefore, that the change of the concentration of ferric chloride, within the limit of the experiment, can hardly be taken the cause of the reaction. From this it does not seem probable that the decomposition electromotive force is so very much changed by changing the concentration of the solution of ferric chloride ten times or so.

When the salt decomposes without any external force being applied, the value of π is zero: then,

$$C^{\frac{3}{2}}_{Fe^{\cdot\cdot}} / \beta = 1{\cdot}4 \times 10^{-11}(1 - KC^{\frac{1}{2}}_{Fe^{III}})C^{2}_{Fe^{III}}.$$

By this formula, the limit of concentration of ferrous salt in the solution above which some force must be applied for the decom-

position, is known. Hence, it seems hardly probable that, within the limit of concentration experimented upon by Spring, the concentration of ferrous salt reaches a degree which is sufficient to give the precipitation with ferricyanide.

Action of ferric nitrate and sulphate upon potassium ferricyanide.

The electromotive force required for the anodic separation of oxygen from a normal solution of the hydrogen ion is according to Nernst and others,[1] 1·08 volts, and that for the anodic separation of chlorine, from a normal solution of the chlorine ion, 1·13 volts. Therefore, it is interesting to compare the reaction between ferric chloride and potassium ferricyanide with that between ferric nitrate and sulphate and the ferricyanide. From the experiment with the solution of aluminium sulphate, already mentioned, its concentration, in which the nitrate or sulphate gives a blue colouration with potassium ferricyanide, is nearly the same with that in which the chloride reacts. It is, therefore, very probable that the reaction of ferric salts in less concentrated solutions of different salts, is connected with the evolution of oxygen and not with that of chlorine. In more concentrated solutions of the salts, ferric chloride gave a more intense colouration than did the sulphate or nitrate. Potassium ferricyanide also gives a more intense colouration to the concentrated solution of ferric chloride than to that of the nitrate or sulphate. This makes it seem probable that, in the concentrated solutions, a force which induces the reaction under consideration is strong enough to liberate chlorine. From an inspection of the experiments under I., it looks also as if the force is a function of the valency of the metals forming the salts.[2] So far as the experiment has been carried out, there is very little evidence to

Nernst, Ber. d. chem. Gesell., **30**, 1547 (1897): Bose, Zeitschr. f. Elektrochem., **4**, 153 (1898): Glaser, ibid., **4**, 355 (1898), and others.

For a very concentrated solution of ferric chloride, the decomposition electromotive force of chlorine should not be far from that of oxygen.

support the theory that the change in the decomposition electromotive force, due to a change in the concentration of the solution of ferric chloride, is the cause under consideration.

V. The reaction proceeds by the removal of ferrocyanide from the system of the equation,

$$2K_3Fe(CN)_6 + 2MCl \rightleftarrows MK_3Fe(CN)_6 + Cl_2$$

The reaction between ferric chloride and potassium ferricyanide may take place by the precipitation of ferrocyanide; or the precipitation may occur from the action of an electrolyte upon the colloidal ferric ferrocyanide. There have been several investigations prosecuted concerning the reduction of potassium ferricyanide. Lessen[1] shows that it is reduced in a hydroiodic acid solution, giving off iodine. This reaction is so complete that it may be used in a volumetric analysis. Meldrum[2] observed also that the ferricyanide is reduced in the presence of fluosilicic acid, Prussian blue being formed thereby.

VI. The reaction proceeds as the result of the removal of chlorine from the system of the equation given in V.

It is possible that the reaction occurs as the result of the removal of chlorine from the system; but the experiment and discussion given in II. will be applicable in this case as well, and after brief consideration it will be seen that there is not much probability of this being the cause of the reaction.

VII. The reaction occurs as the result of the increase of a chloride (MCl) in the system of the equation given in V.

The presence of a chloride (MCl), according to the equation

[1] Lieb. Ann., **91**, 240, (1854).
[2] Chem. News, **78**, 269, (1898).

given in V., may induce the reaction; but according to the equations,

$$3FeCl_2 + 2K_3Fe(CN)_6 = Fe_3(Fe(CN)_6)_2 + 6KCl, \text{ and}$$
$$4FeCl_3 + 3MK_3Fe(CN)_6 = Fe_4(Fe(CN)_6)_3 + 3MCl + 9KCl,$$

it must rather hinder that reaction. At a higher temperature, as observed by Matsuschek,[1] the ferricyanide itself in the solution is reduced in the presence of ammonium chloride; but the presence of a chloride does not seem to have much effect upon the present reaction, as its absence—so far as the experiment is concerned—has been proved to have very little influence upon the range of the concentration of the solution in which the reaction is visible.

In highly concentrated solutions, however, the blue colouration, as has been already mentioned, is more intense in the presence of a chloride than in its absence. This phenomenon may be explained as the result of such an increase of a force causing the reaction to take place, that it is strong enough to give chlorine in addition to oxygen.

VIII. The precipitation of ferrous ferricyanide becomes possible by increasing the concentration of potassium ferricyanide: or, in the equation given in V., the concentration of ferrocyanide becomes sufficient for the precipitation of Prussian blue.

In solutions of potassium ferricyanide of different concentrations up to saturation, as has already been mentioned, ferric chloride does not give a blue colouration. It is, therefore, very probable that the effect, as given under the present caption, plays very little part, if any, in the reaction under consideration.

IX. The presence of dust in the reagents or in the water used for the preparation of the solution, causes the reduction of the two salts, and the reaction under consideration results.

[1] Chem. Ztg., **29**, 439, (1905).

Experiments were made by carefully filtering the solution, but no difference was observed from those which otherwise corresponded. Moreover, the evolution of chlorine and the regularity of the relations within the limits of concentration of the solutions, in which the reaction under consideration is visible, can hardly be accounted for as the effect of dust.

A comparison of the reducibility of ferric chloride and of potassium ferricyanide.

In all that has been said, the reaction under consideration was based on two equations:

$$2FeCl_3 \rightleftarrows 2FeCl_2 + Cl_2$$
$$2K_3Fe(CN)_6 + 2MCl \rightleftarrows 2K_3MFe(CN)_6 + Cl_2.$$

It was supposed, also, that these reactions are equally likely to take place. However, there must be a difference between them. Their reducibility may be measured by the electromotive force which is to be produced in their reduction. Bancroft[1] gives 0·255 as the difference, and Neumann,[2] 0·254; that of ferric chloride is reduced more easily than potassium ferricyanide. From this point of consideration, it is very probable that, in the reaction under consideration, the reduction of ferric chloride will take place in a greater degree than does that of ferricyanide.

To determine whether ferric chloride or potassium ferricyanide is much more reduced in the present reaction, it is necessary to know, in addition to the voltage produced in the reduction, the relative tendency to the formation of ferric ferricyanide and ferrous ferricyanide. According to Hofmann and others,[3] however, the blue precipitates formed by the action of ferric salt upon ferrocyanide and of ferrous salt upon ferricyanide, seem identical. This makes it difficult to decide which reduction took place in a greater degree.

1 Zeitschr. f. physik Chem., **10**, 387, (1892).
2 Ibid., **14**, 228, (1894).
3 Lieb. Ann., **337**, 1 (1904); **340**, 267 (1905); **352**, 54 (1906).

Summary and Conclusion.

Experiments show that potassium ferricyanide reacts with ferric chloride, not only in the concentrated solution of the latter but also in that of many other salts. In the latter case, there is a regular connection between the concentration, in which the reaction takes place, and the valency of the metals which form the salts. To account for the phenomenon, several assumptions were made and discussed. The conclusion reached is that it is probable that the precipitation of Prussian blue by the salts plays a most important part in the reaction. The reaction of ferric nitrate and sulphate upon potassium ferricyanide seems, also, to prove this opinion. Spring's explanation, that the reaction under consideration is caused by the decomposition of ferric chloride due to a change in the concentration, appears to be hardly plausible.

Chemical Laboratory,
Higher Technological School of Tokyo.

Kinetics of Two Simultaneous Reactions in a System.

By

Kozo Ikawa.

Theoretically, it may be expected that, when a number of reactions takes place in any system, each proceeds as if it were independent of the others; each obeying the law of mass action. Coppadoro[1] has shown that if a solution of cane sugar and methyl acetate mixed is treated with hydrochloric acid, the hydrolysis of each substance takes place in the mixture independently of the other.

Cohen[2] has studied the decomposition of a mixture of dibromosuccinic and isodibromosuccinic acids, and has shown that the reaction velocity is not in accordance with the equation,

$$-\frac{dC}{dt}=kC,$$

where k and C are the velocity coefficient and the total concentration of the acids respectively, because the reaction velocity must be expressed by the equation,

$$-\frac{dC}{dt}=k_1C_1+k_2C_2,$$

where k_1 and k_2 are the velocity coefficients of the two reactions, and C_1, C_2 the concentrations of the two acids at the time t.

In order to verify the last equation in another case, the author has chosen a mixture of two different esters, and has studied their decomposition by acids.

[1] Chem. Centralb., **72**, II, 386 (1901).

[2] Studien zur chem. Dynamik., S. 117.

The velocity of hydrolytic decomposition of an ester of a weak acid by catalytic action of a strong acid, as is well known, may be expressed by the following equation,

$$\frac{dx}{dt}=k(a-x),$$

where the symbols have the usual meanings.

On integration, it gives,

$$k=\frac{1}{t}\ln\frac{a}{a-x},$$

or

$$x=a(1-e^{-kt}).$$

When a mixture of two different esters is hydrolysed by an acid, and each proceeds independently of the other, we have for both reactions, the following equations respectively:

$$\frac{dx}{dt}=k(a-x),$$

$$\frac{dy}{dt}=k'(a'-y),$$

where a and a' are the initial concentrations of the esters, x and y the decrease of the concentration at the time t, and k and k' the velocity coefficients of the reactions respectively. On integration, we have:

$$x=a(1-e^{-kt}),$$
$$y=a'(1-e^{-k't}).$$

Let z denote the total concentration of the esters decomposed at the time t; then we have:

$$z=x+y$$
$$=a(1-e^{-kt})+a'(1-e^{-k't}).$$

To verify this equation, the following experiments were conducted.

(A) Methyl and Ethyl Acetates.

A flask of the capacity of about 50 c.c. was well steamed, and 40 c.c. of half-normal hydrochloric acid solution were introduced into it, and then it was stoppered with a paraffinised cork. It was kept in a thermostat at 25°. 2 c.c. of an ester were subsequently added, the flask well shaken, and 2 c.c. of the mixture were immediately taken out and titrated with baryta water of $^1/_{10}$—$^1/_{20}$ normal. A similar process of titration was repeated at stated intervals. In the case of a mixture of the two esters, the experiments were carried out as follows: 20 c.c. of methyl acetate were diluted to 100 c.c. with distilled water free from carbonic acid. 20 c.c. of the solution of methyl acetate so prepared and 20 c.c. of ethyl acetate were added to the normal hydrochloric acid, and the experiments were proceeded with as in the case of a single ester. Thus, the following results were obtained:

(*a*) *Methyl acetate.*

Table 1.

t (min.)	Titration.	$\log\frac{a}{a-x}$	k
0	10·30		
20	10·86	0·02997	0·00346
40	11·57	0·06034	0·00347
70	12·84	0·10629	0·00349
100	13·40	0·15093	0·00347
130	14·16	0·19603	0·00347
160	14·87	0·24070	0·00346
200	15·73	0·30326	0·00349
240	16·46	0·36446	0·00350
280	17·10	0·42549	0·00350
300	17·38	0·45589	0·00350
∞	21·285	—	—
		Mean:	0·00348

Table 2.

t (min.)	Titration.	$\log\frac{a}{a-x}$	k
0	10·32		
20	11·07	0·03028	0·00348
40	11·74	0·06039	0·00347
70	12·70	0·10555	0·00347
100	13·60	0·15287	0·00352
130	14·38	0·19665	0·00348
170	15·28	0·25787	0·00349
210	16·06	0·31693	0·00348
250	16·76	0·37763	0·00348
300	17·62	0·45354	0·00348
350	18·15	0·53111	0·00349
∞	21·42	—	—
		Mean:	0·00349

Table 3.

t (min.)	Titration.	$\log\frac{a}{a-x}$	k
0	10·28		
20	11·03	0·03002	0·00346
40	11·73	0·05992	0·00345
70	12·70	0·10519	0·00346
100	13·62	0·15270	0·00352
130	14·34	0·19450	0·00345
170	15·30	0·25666	0·00348
210	16·12	0·31784	0·00349
250	16·80	0·37629	0·00347
300	17·55	0·45127	0·00346
350	18·20	0·52871	0·00348
∞	21·53	—	—
		Mean:	0·00347

As is seen from the above tables, the mean value of the velocity coefficient is as follows:

$$k = 0{\cdot}003480$$

(*b*) *Ethyl acetate.*

Table 4.

t (min.)	Titration.	$\log \frac{a}{a-x}$	k'
0	10·36		
20	10·91	0·02978	0·00343
40	11·41	0·05874	0·00338
70	12·12	0·10350	0·00340
100	12·76	0·14823	0·00341
130	13·33	0·19235	0·00341
170	13·98	0·24883	0·00337
210	14·59	0·30949	0·00339
250	15·12	0·37008	0·00341
280	15·55	0·42632	0·00338
∞	18·66	—	—
		Mean:	0·00340

Table 5.

t (min.)	Titration.	$\log \frac{a}{a-x}$	k'
0	10·30		
20	10·86	0·03002	0·00346
40	11·37	0·05975	0·00344
70	12·07	0·10389	0·00342
100	12·69	0·14728	0·00339
130	13·26	0·19091	0·00338
170	13·96	0·25148	0·00341
210	14·54	0·30893	0·00339

t (min.)	Titration.	$\log \frac{a}{a-x}$	k'
250	15·04	0·36638	0·00338
290	15·50	0·42595	0·00338
∞	18·62	—	—
		Mean :	0·00340

Table 6.

t (min.)	Titration.	$\log \frac{a}{a-x}$	k'
0	10·30		
20	10·85	0·02956	0·00340
40	11·36	0·05877	0·00338
70	12·06	0·10266	0·00338
100	12·70	0·14687	0·00338
130	13·29	0·19241	0·00341
170	13·95	0·24953	0·00338
200	14·40	0·29310	0·00337
250	15·07	0·36720	0·00338
300	15·63	0·44136	0·00339
350	16·11	0·51566	0·00339
400	16·50	0·58736	0·00338
∞	18·66	—	—
		Mean :	0·00339

From the data given above, the following mean value is obtained :

$$k' = 0{\cdot}003397.$$

(*c*) *A mixture of methyl and ethyl acetates.*

Table 7.

$a = 11{\cdot}185$ c.c. $a' = 9{\cdot}585$ c.c.

t (min.)	Titration.	z (obs.)	Calc. x	Calc. y	Calc. $x+y$	Diff.
0	11·93	—	—	—	—	—
20	13·33	1·40	0·75	0·63	1·38	0·02
50	15·30	3·37	1·80	1·48	3·28	0·09
70	16·27	4·34	2·27	1·99	4·26	0·08
100	18·09	6·16	3·15	2·90	6·05	0·11
130	19·43	7·50	3·95	3·48	7·43	0·07
160	20·98	9·05	4·60	4·31	8·91	0·14
200	22·34	10·41	5·33	4·99	10·32	0·09

Table 8.

$a = 11{\cdot}061$ c.c. $a' = 9{\cdot}49$ c.c.

t (min.)	Titration.	z (obs.)	Calc. x	Calc. y	Calc. $x+y$	Diff.
0	12·15	—	—	—	—	—
20	14·01	1·86	1·04	0·88	1·92	0·06
40	14·83	2·68	1·44	1·21	2·65	0·03
72	16·84	4·69	2·52	2·08	4·60	0·09
100	18·27	6·12	3·44	2·53	5·97	0·15
130	19·64	7·49	4·15	3·27	7·42	0·07
160	20·92	8·77	4·80	3·89	8·69	0·08
200	22·42	10·30	5·79	4·41	10·20	0·10

As is seen, the calculated values of z are, within the limits of experimental errors, in satisfactory agreement with the experimental values.

(B) Ethyl Acetate and Butyrate.

With methyl and ethyl acetates, the velocity coefficients of the hydrolytic decomposition were not greatly different from each other; therefore the author has next taken ethyl acetate and ethyl butyrate, in which the velocity coefficients are considerably different. As the solubility of ethyl butyrate in water is comparatively small, it was weighed in a sealed glass bulb that was broken in the midst of a $^1/_{10}$ normal hydrochloric acid solution, of which so much was taken as to make the concentration of the ester solution $^1/_{10}$—$^1/_{20}$ normal. Then, the experiment was carried out in the same way as in the case of (A). The results were as follows:

(*d*) *Ethyl butyrate.*

Table 9.

t (min.)	Titration.	$\log \frac{a}{a-x}$	k'
0	22·23	—	—
1020	24·54	0·18743	0·000423
1420	25·39	0·25848	0·000419
2400	26·71	0·43413	0·000417
2700	27·02	0·48874	0·000417
∞	29·23	—	—
		Mean:	0·000419

Table 10.

t (min.)	Titration.	$\log \frac{a}{a-x}$	k'
0	25·67	—	—
250	26·26	0·04562	0·000420
1250	28·03	0·22573	0·000416
1700	28·63	0·30780	0·000417
2110	29·61	0·48997	0·000416
∞	31·50	—	—
		Mean:	0·000417

Table 11.

t (min.)	Titration.	$\log \frac{a}{a-x}$	k'
0	25·70	—	—
250	26·29	0·04608	0·000424
1250	28·06	0·22599	0·000416
1650	28·62	0·30197	0·000421
2700	29·65	0·49379	0·000421
∞	31·52	—	—
		Mean:	0·000420

From the data given above, the mean value of the velocity coefficient was found to be:

$$k' = 0.000419.$$

(*e*) *Ethyl acetate.*

Table 12.

t (min.)	Titration.	$\log \frac{a}{a-x}$	k
0	25·10	—	—
110	25·92	0·03302	0·000693
300	27·19	0·08970	0·000688
1310	31·79	0·39504	0·000694
1700	32·85	0·51140	0·000693
∞	36·30	—	—
		Mean:	0·000692

Table 13.

t (min.)	Titration.	$\log \frac{a}{a-x}$	k
0	26·20	—	—
170	26·45	0·05140	0·000696
360	27·68	0·10870	0·000695
1370	32·08	0·51374	0·000695

t (min.)	Titration.	$\log \frac{a}{a-x}$	k
1760	33·08	0·52808	0·000691
∞	36·40	—	—
		Mean:	0·000694

Table 14.

t (min.)	Titration.	$\log \frac{a}{a-x}$	k
0	25·20	—	—
300	26·97	0·09061	0·000697
1450	31·13	0·43280	0·000690
1700	31·69	0·50924	0·000692
2800	33·20	0·82700	0·000682
∞	34·60	—	—
		Mean:	0·000690

The mean value of the velocity coefficient is obtained as follows:

$$k = 0{\cdot}000692.$$

(*f*) *A mixture of ethyl acetate and ethyl butyrate.*

Table 15.

Volume of 1/10 normal hydrochloric acid	60 c.c.
Weight of ethyl acetate	0·2386 gr.
Weight of ethyl butyrate	0·2174 gr.

t (min.)	Titration.	z (obs.)	Calc. x	Calc. y	Calc. $x+y$	Diff.
0	22·16	—	—	—	—	—
200	23·82	1·66	1·15	0·50	1·65	0·01
350	24·77	2·61	1·92	0·84	2·76	0·15
1290	29·96	7·80	5·27	2·57	7·85	0·05
1750	31·53	9·37	6·27	3·20	9·47	0·10

Table 16.

Volume of 1/10 normal hydrochloric acid	70 c.c.
Weight of ethyl acetate	0·2691 gr.
Weight of ethyl butrate	0·2808 gr.

t (min.)	Titration.	z (obs.)	Calc. x	Calc. y	Calc. $x+y$	Diff.
0	22·16	—	—	—	—	—
200	23·82	1·66	1·12	0·55	1·67	0·01
350	24·94	2·78	1·87	0·93	2·80	0·02
1290	30·09	7·93	5·13	2·86	7·99	0·06
1750	31·78	9·62	6·09	3·56	9·64	0·02

Thus, the agreement between the calculated and the observed values is quite satisfactory, so that the verification is competent.

Oxidation of Hydroquinone by the Catalysis of Carbon.

By

Motooki Matsui.

The fact that charcoal possesses the property of absorbing many times its own volume of various gases, and as a consequence, often accelerates the reaction between gaseous substances, has been universally known for a long time. Its action as a conveyer of oxygen to the gaseous products emanating from substances which are in a state of putrefaction, was first studied by J. Stenhouse,[1] who observed that all gases and vapours evolved from a putrefying animal buried in charcoal were completely oxidized, so that no unpleasant odour was perceptible. Induced by this memorable discovery, F. Cr. Calvert[2] made a series of experiments, and succeeded in obtaining the products of oxidation from sulphur dioxide, sulphuretted hydrogen, phosphoretted hydrogen, ethyl alcohol, amyl alcohol, ethylene and propylene, which were brought into contact with boxwood charcoal saturated with oxygen. Since that time, similar new facts have been successively discovered, the oxidation of leucaniline in its alcoholic solution by W. Hofmann,[3] that of α-naphthylamine, paraphenylenediamine, and the colouring matter of wine by P. Cazeneuve,[4] and that of the oxyacids, such as citric acid or mandelic acid, and glycerine by H. Freundlich.[5]

[1] Ann. d. Chem., **90**, 186.
[2] Journ. chem. Soc., **20**, 293; Journ. pr. Chem., **101**, 397.
[3] Ber. d. chem. Ges., **7**, 530.
[4] Compt. rend. **110**, 788; Journ. chem. Soc., **58**, 690.
[5] Zeitschrift f. physik. Chem., **57**, 458.

Now, the author, who has ever noticed that hydroquinone is readily oxidised by contact action of charcoal, has conducted a series of experiments with the object of closely investigating the phenomena of oxidation. The following statements are the outlines of the experiments so carried out.

Oxidation proceeds in the moist state at ordinary temperature.

When hydroquinone and charcoal (animal charcoal of the purest quality, from Merck), moistened with a small quantity water, were rubbed together in a mortar, the mixture at once became coated with green-coloured quinhydrone.

Oxidation takes place in an aqueous, alcoholic, or etherial solution at ordinary temperature.

A small quantity of charcoal was added to a 3% aqueous solution of hydroquinone and the mixture stirred, when the solution immediately assumed a reddish-brown colour, and after a while green crystals of quinhydrone separated at the surface. The same experiment was repeated with an alcoholic as well as with an etherial solution; with the former, the oxidation was observed to take place nearly in the same degree as in the aqueous solution; with the latter, however, in only a very slight degree. In order to determine such points of difference quantitatively, the following experiment was conducted: 300 c. c. of water and of 90% alcohol were taken separately in two evaporating dishes of the same capacity, and to each of them five grams of hydroquinone and one gram of charcoal were added. After standing fo twenty minutes, the respective quantities of quinone formed were determined by Valeur's method.[1] The results were as follows:

[1] Compt. rend., **129**, 552; Centr. Blatt., 1899, II, 906.

Quinhydrone in the aqueous solution was first extracted with ether, and on evaporating the ether, it was redissolved in 90% alcohol so as to make it suitable for the determination.

	1/10 N. Sod. thiosulphate.	Quinone.
In alcoholic solution	22·5 c. c.	0·12 grm.
In aqueous solution	21·6 „	0·12 „

Oxidation takes place only with access of air.

In his paper above-referred to, Hofmann states that leucaniline is oxidised by the oxygen contained in the pores of the charcoal; in the present case, also, the oxidation was at first ascribed to the same cause. The results of the experiments show, however, that this reasoning would certainly not suffice to explain this instance of oxidation. An aqueous solution of hydroquinone, with some charcoal, was introduced into a glass tube which was sealed after the air contained in it had been replaced by carbon dioxide. The tube was now heated for a few hours over a water bath; but no perceptible indication of oxidation was observed, the solution remaining colourless and even on cooling, not a particle of quinhydrone crystallising out. The tube was then opened and allowed to stand at the ordinary temperature, whereupon the surface of the solution in the tube gradually became reddish-brown and quinhydrone began to crystallise along the wall of the tube at the surface of the solution. Judging from this result, we can hardly doubt that the oxygen which plays a principal part in the oxidation in question, is that of the air, and not the oxygen which has previously been absorbed in the pores of the charcoal. If this view be correct, the rate of oxidation ought to differ according to the area of the surface of the solution exposed to the air. In order to confirm this contention, another experiment was conducted, as follows: into each of an evaporating dish and a flask, five grams of hydroquinone, one gram of charcoal and 300 grams of water were introduced (the surface of the solution in the flask being kept at its neck), and after standing for twelve hours at the ordinary temperature, the quantity of quinone was determined by the aforementioned method. As was expected, more quinone was found in the dish than in the flask.

	1/10 N. Sod. thio-sulphate.	Quinone.
In the flask	15·0 c.c.	0·08 grm.
In the dish	26·7 „	0·15 „

At higher temperature, oxidation proceeds more quickly.

Five grams of hydroquinone, one gram of charcoal, and 200 grams of water were introduced into a flask which was connected with an inverted condenser and a delivery tube: the flask was heated over a water bath for three hours with a constant supply of air through the delivery tube. A similar experiment was performed with an alcoholic solution, as well as with an etherial solution, of the same dilution, and the following results were obtained:

	1/10 N. Sod. thio-sulphate.	Quinone.
In the aqueous solution	64·0 c.c.	0·35 grm.
In the etherial solution	30·2 „	0·16 „
In the alcoholic solution	As quinone further acts upon alcohol to oxidise it into aldehyde, the exact quantity of it could not be determined.	

As is seen in some other catalyser, the activity of animal charcoal as an oxidising catalyser gradually lessens as it is repeatedly used, though this is recovered when the charcoal is well washed and dried. Finely powdered wood charcoal was also found to have a similar but very feeble catalytic action.

Summary.

1. Animal charcoal acts catalytically to oxidise hydroquinone.

2. With an aqueous or alcoholic solution, the oxidation readily takes place at ordinary temperature; with an etherial

solution, however, a smooth oxidation is observable only when the solution is heated over a water bath with a constant supply of air.

3. Oxidation takes place only with access of air; therefore, in an exhausted sealed tube the oxidation phenomenon is not observed.

June, 1908.

Isomeric Phenylphthalimides and Some Allied Compounds.

By

Mitsuru Kuhara and **Shigeru Komatsu.**

Several years ago one of the present authors in collaboration with Fukui[1] observed the formation of *a*-phenylphthalimide,—so-called upon the assumption of the unsymmetrical nature of its structure,—from phthalyl chloride and aniline. Hoogewerff and van Dorp[2] having, however, repeated Kuhara and Fukui's experiments, claim that *a*-phenylphthalimide is a mixture of phthalanilide and normal phenylphthalimide, but the so-called phthalophenylisoimide, which is said to have been previously prepared by van der Meulen[3] by treating phenylphthalamic acid with acetyl chloride, is the real unsymmetrical phenylphthalimide. Dunlap and Cummer also side with Hoogewerff and van Dorp in contending for the non-formation of *a*-phenylphthalimide from phthalyl chloride and aniline.

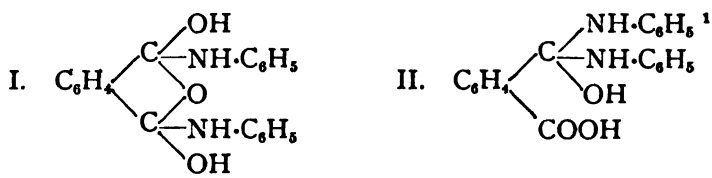
The authors have, likewise, repeated Kuhara and Fukui's experiments; but have not been able to isolate the same substance again, although it was done before. Hence, it is strange that, in the previous experiments, just exactly the right conditions for its formation should have been found, and that such conditions cannot again be met with.

By using solutions of phthalyl chloride and aniline, each dissolved in 95% alcohol, the simultaneous formation of three

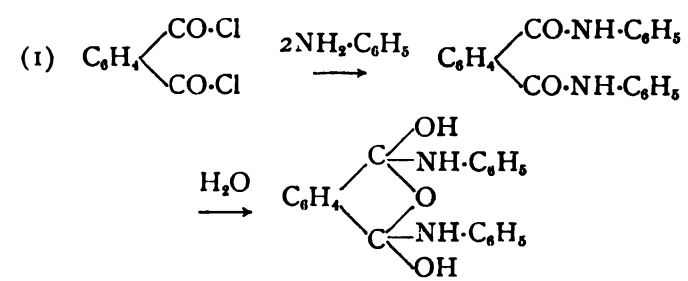
[1] Amer. Chem. Journ., **26**, 456.
[2] Rec. trav. chim., **21**, 339.
[3] Ibid., **15**, 286.

substances was observed; that is, phthalanilide, the normal phenylphthalimide, and a new substance which corresponds in composition to a hydrated phthalanilide, $C_{20}H_{16}N_2O_2 \cdot H_2O$, and possesses a melting-point of 175°–176°. It behaves as a dibasic acid forming salts corresponding to $C_{20}H_{16}M'_2N_2O_3$ and $C_{20}H_{16}M''N_2O_3$. It does not give up water, therefore the latter is considered to be the water of constitution, but not the water of crystallization.

Now, with regard to the constitution of the new substance, there should be assignable one of the two possible formulas:



Suppose that the new substance possesses a constitution corresponding to formula I, then it should be derived from the normal phthalyl chloride according to the following scheme of reaction:

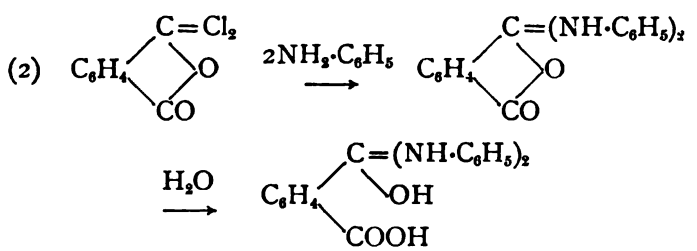


Then, the new substance ought to be produced, as this scheme shows, from the normal phthalanilide by assimilating a molecule of the water present in alcohol. It is, however, not only very

[1] The possibility of the existence of a substance having such a constitution, was lately predicted by Tingle and Lovelace—Amer. Chem. Journ., 38, 644.

improbable that the acid amides or substituted acid amides will yield acids by simple hydration, while they are known to be converted into so-called pseudo acids, only in the form of salts as the result of tautomerisation under the action of a base, but also it was found by experiments, that the same substance is never formed actually from the normal phthalanilide by the action of water or aqueous alcohol at ordinary as well as low temperature.

If the new substance, however, be assumed to have a constitution corresponding to formula II, it ought to be formed from the unsymmetrical phthalyl chloride, as will be shown in the following scheme of reaction:

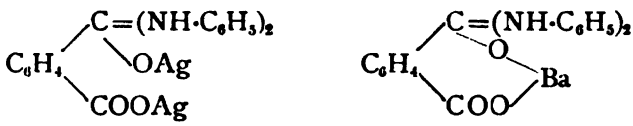


And that the new substance will be produced from the unsymmetrical phthalanilide, as scheme (2) indicates, can be explained upon the assumption that the unsymmetrical phthalanilide, as it takes the form of an inner anhydride of the lactone type, is possible to change to an acid by hydration.

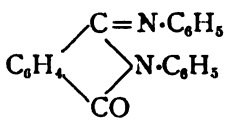
Hence, it is highly probable that the new substance possesses the constitution represented by formula II, assuming that phthalyl chloride may partly take an unsymmetrical form of structure at low temperature, just as one of the present authors and Fukui[1] have already stated. Therefore, it is designated by the name *a-Dianilinophthalic Acid.* Its dibasic nature may be explained by

[1] Amer. Chem. Journ. **26**, 462.

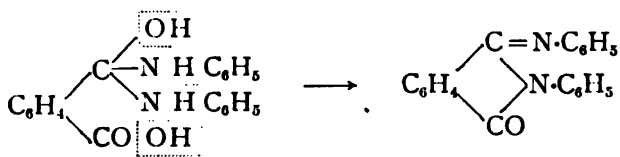
assuming the constitution of silver and barium salts to correspond respectively to the following formulas:



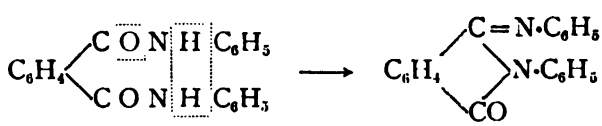
The view for the unsymmetrical structure of the new acid, is further supported by the fact that it yields a dianil,[1] which had already been obtained by von Gerichten from phthalyl tetrachloride and aniline, and which is said to have the constitution,



This substance was observed by the authors to be formed by the action of a dehydrating agent, such as acetyl chloride or phosphorous pentachloride, upon *a*-dianilinophthalic acid; the reaction being shown by the following scheme:



Again, it was found that the normal phthalanilide actually yields the same substance by the action of the same dehydrating agents under the same conditions; the reaction possibly being:

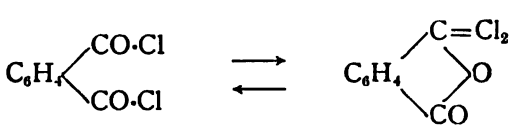


[1] Ber. d. chem. Gesell., **13**, 420.

This reaction must evidently be analogous to the formation of orthosulphobenzdianil and paranitrosulphobenzdianil from orthosulphobenzanilide and paranitrosulphobenzanilide respectively, as shown by Remsen[1] and Henderson.[2]

Then, there occurs the question, whether or not the new substance may possibly possess the symmetrical structure, I, and yield the normal phthalanilide at first and subsequently von Gerichten's dianil, by the action of a dehydrating agent? Such possibility, however, is denied without hesitation, because the formation of the dianilino acid of the symmetrical structure has already been disproved.

Now, inferring, from the simultaneous production of phthalanilide, the normal phenylphthalimide and *a*-dianilinophthalic acid by the interaction of phthalyl chloride and aniline, both cooled to $-10°$, we are led to the opinion that phthalyl chloride, which should possess the normal constitution at ordinary temperature, may be transposed into the isomeric chloride of the unsymmetrical constitution on lowering of temperature; so that both may exist simultaneously, as a mixture, at certain low temperatures, but the change may be reversed on elevating the temperature, so as to be,



Again, it is strange that, although the authors made repeated efforts to get possession of van der Meulen's phthalophenylisoimide from phenylphthalamic acid by the action of acetyl chloride, they all failed so that, not a bit of it could have been obtained. However, every time the experiment was repeated, a pale-yellow

[1] Amer. Chem. Journ. **18**, 815.
[2] Ibid, **25**, 22.

crystalline substance was found to be produced; but its melting point varied, with the different experiments, between 93° and 125°. For the purpose of purifying the substence by repeated recrystallization from its etherial solution, the latter was allowed to stand by itself, for some time for spontaneous evaporation, during which the normal phenylphthalimide always crystallized out first and then an amber-coloured substance. On repeating the same operation again and again, a quantity of the normal phenylphthalimide always separated previously to the appearance of the amber-coloured substance; but upon continuing the repetition of the process, eventually amber-coloured rhombic prisms alone crystallized out from the etherial solution, giving no more normal phenylphthalimide. Their melting-point was found to be 125°–126°. Hence, it was thought that, besides the amber-coloured compound, there must be contained in the reaction product a substance which would readily change to the normal phenylphthalimide.

Now, upon evaporating the etherial solution of the direct reaction product as quickly as possible, a substance consisting of almost colourless needles was isolated before the amber-coloured compound crystallized out, and on repeating its recrystallization from the etherial solution the substance was obtained in a pure state, as was inferred from the constancy of its melting point, 83°–84°. This new substance and the aforementioned amber-coloured compound are both isomeric with phenylphtalimide, by inference from the results of their analysis; but both of them are evidently different in properties from Kuhara and Fukui's *a*-phenylphthalimide[1] as well as from van der Meulen's phthalo-phenylisoimide.[2]

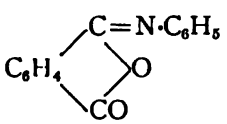
Consequently, the pale-yellow substance, or direct reaction product obtained from phenylphthalamic acid by the action of acetyl chloride, must be a mixture of a compound, crystallizable in

[1] Loc. cit.
[2] Loc. cit.

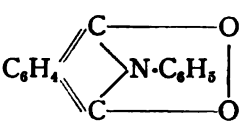
amber-coloured rhombic prisms and fusible at 125–126°, with the substance which crystallizes in almost colourless, fine needles, and possesses a lower melting-point, 83–84°, being so unstable as to change readily into the normal phenylphthalimide, probably by intramolecular rearrangement. The authors, then, wonder if the phthalophenylisoimide obtained by van der Meulen[1] may be the same mixture of two isomeric substances above described, but not a definite compound, because he states that it melts at 115–116°,[2] while Hoogewerff and van Dorp[3] describe it as melting at 120–122°. Such discrepancies in the statements on record seem to be due to the indefinite nature of the substance, or rather to say, to the mixture of two isomeric substances, as hereinbefore stated.

With regard to the structure of the isomeric modifications of the phenylphthalimide, the following two formulas are possible:

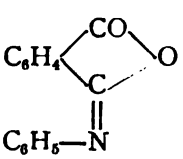
I.



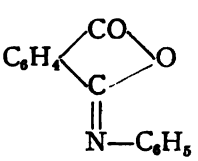
II.



and of the former, still two stereoisomers are possible:



Syn-form.



Anti-form.

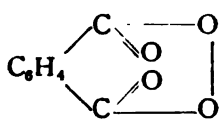
As to the nature of one of the new substances, or the amber-

[1] Loc. cit.

[2] Rec. trav. chim., **15**, 286.

[3] Ibid., **21**, 341.

coloured compound, the authors are not yet quite certain; but they are of the opinion that it may possess a constitution corresponding to the formula, II, by inference from its behaviour. By heating its acetic acid solution in a sealed tube at 120°, it changes to the normal phenylphthalimide, partly decomposing into aniline and phthalic acid. Crystals, held on the loop of a platinum wire, when heated suddenly in the flame of a Bunsen burner, gently detonate, showing some likeness to phthalyl superoxide,[1]



Further, the coloured nature of the substance is, possibly, due to the quinoide (ortho) form of its molecular constitution.

The second new substance, crystallizing in colourless fine needles (melt. point 83–84°) may be an isomeric phenylphthalimide of unsymmetrical structure, by inference from its behaviour; such as to change to the isomeric normal phenylphthalimide, with excessive readiness simply in its etherial or alcoholic solution, or on slightly heating by itself. The authors designate it by the name of *β-a*-phenylphthalimide, in distinction from *a*-phenylphthalimide, previously obtained by one of them and Fukui.

The actual existence of two stereoisomeric unsymmetrical phenylphthalimides, corresponding to the syn and anti forms already mentioned, is possible. The authors, now, put forward the explanation of the existence of more than one unsymmetrical phenylphthalimides upon the assumption that *β-a*-phenylphthalimide may possess one of two steroisomeric forms, and that if one of two other phenylphthalimides, that is Kuhara and Fukui's *a*-phenylphthalimide and van der Meulen's phthalophenylisoimide, the existence of both of which is now under discussion,

[1] Ber. d. chem. Gesell., **27**, 1511.

is not declared not to exist in reality, it may have the other form of the two.

EXPERIMENTAL.

1. *a-Dianilinophthalic Acid,* $C_6^2H_4 \begin{cases} C=(NH\cdot C_6H_5)_2 \\ OH \\ COOH. \end{cases}$

Alcoholic solution of phthalyl chloride (1 mol.) was cautiously added, drop by drop, to an alcoholic solution of aniline (4 mols.), each dissolved in 95% alcohol, the mixture being constantly stirred, and both solutions having been cooled to −10° in a freezing mixture of ice and salt. After each addition of the phthalyl chloride solution, there was produced a heavy white precipitate. The whole mixture was allowed to stand for a few hours in the freezing mixture, and then the precipitate was separated from the liquid by filtration; it was washed with alcohol and made to recrystallize from the warm alcoholic solution. The substance thus obtained, has all the properties of phthalanilide, prepared by Rogow,[1] van der Meulen,[2] and by Dunlap and Cummer.[3]

The filtrate from phthalanilide deposited a white crystalline precipitate on standing over night. It was purified by recrystallization from alcohol, and the new substance thus obtained, or so-called *a*-dianilinophthalic acid, was found under the microscope to consist of an aggregation of rhombic crystals and to melt at 175–176°. It is insoluble in water, ether, chloroform, and benzene, but slightly soluble in alcohol. From the mother liquor, the normal phenylphthalimide separated out, on standing for a while.

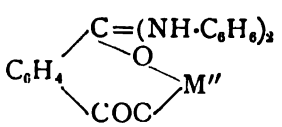
[1] Ber. d. chem. Gesell., **30**, 1443.
[2] Rec. trav. chim., **15**, 286.
[3] Journ. Amer. Chem. Soc., **25**, 620.

The new substance was analysed and the results are given below :—

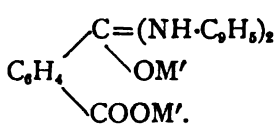
I.	0·2	grm. the substance	gave	0·5272	grm.	CO_2	and	0·102	grm.	H_2O.
II.	0·2	„ „	„	„ 0·5208	„	„	„	0·1031	„	„
III.	0·2	„ „	„	„ 0·5206	„	„	„	0·1053	„	„
IV.	0·2	„ „	„	„ 0·5327	„	„	„	0·0979	„	„
V.	0·5052	„ „	„	„ 0·0436	„	nitrogen.				
VI.	0·4994	„ „	„	„ 0·0420	„	„				

	Calc. for $C_6H_4\begin{cases}C{=}(NHC_6H_5)_2\\OH\\COOH.\end{cases}$	Found. I.	II.	III.	IV.	Mean.
Carbon	71·85	71·89	71·00	71·00	72·65	71·63
Hydrogen	5·38	5·66	5·73	5·83	5·45	5·67
Oxygen	14·39	—	—	—	—	—
		V.	VI.			
Nitrogen	8·38	8·51	8·41	... ...	... ...	8·46

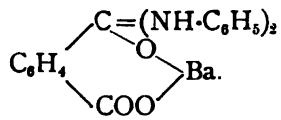
The substance is of unstable nature, so that it is readily decomposed into aniline and normal phenylphthalimide, when it is treated with hot alcohol, acetic acid, or alkali; and also when it is simply heated by itself at 100°. Upon heating with hydrochloric acid, it splits up into aniline, normal phenylphthalimide and phthalic acid. Even after keeping it under an exhausted dessicator over sulphuric acid for a few weeks, dehydration is never effected, but on subjecting it to the action of dehydrating agents, such as phosphorus pentachloride, acetyl chloride, phosphorus pentaoxide, &c., it yields von Gerichten's phthaldianil,[1] the details of which will be described afterwards. It behaves as a dibasic acid forming the salts corresponding to



and

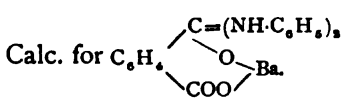


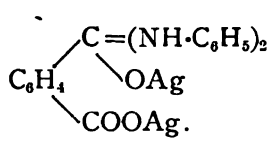
[1] Ber. d. chem. Gesell., **13**, 420.

2. *Barium a-Dianilinophthalate,* 

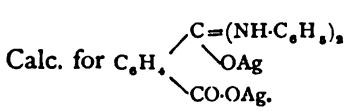
Upon treating the free acid with baryta water, it was found to dissolve freely. The excess of baryta having been removed by means of carbon dioxide, the filtrate from barium carbonate was concentrated by evaporation in vacuum. A slightly yellow-coloured crystalline precipitate, deposited from the concentrated solution, was dried over sulphuric acid and analysed, the results being given below:—

I. 0·2034 grm. the barium salt gave 0·101 grm. $BaSO_4$.
II. 0·2450 „ „ „ „ „ 0·1224 „ „

	Calc. for 	Found. I.	Found. II.
Barium	29·27	29·21	29·37

3. *Silver a-Dianilinophthalate,* 

On adding silver nitrate to the neutral solution of ammonium *a*-dianilinophthalate, there was produced at first, a white, bulky precipitate, which soon changed to a crystalline state. The precipitate, having been well washed and dried over calcium chloride, was analysed; 0·12 grm. of the salt gave 0·0474 grm. of silver.

	Calc. for 	Found.
Silver	39·41	39·54

4. *Phthaldianil*, $C_6H_4 \begin{cases} C=N\cdot C_6H_5 \\ CO \end{cases} N\cdot C_6H_5$.

This substance was first prepared by von Gerichten[1] as a product of the interaction of phthalyl tetrachloride and aniline. The authors observed the production of the same compound from both phthalanilide and *a*-dianilinophthalic acid by the action of phosphorus pentachloride or pentaoxide. When either phthalanilide or *a*-dianilinophthalic acid was mixed with phosphorus pentachloride in unhydrous chloroform as a medium, a reaction immediately took place. On heating the mixture in a flask provided with an inverted condenser, phthalanilide or *a*-dianilinophthalic acid and phosphorus pentachloride gradually disappeared with the evolution of hydrochloric acid forming a yellow solution. Then, the chloroform was removed by distillation, and the residue treated with water to get rid of phosphorus compounds. The substance which was insoluble in water was found to consist of two different compounds, one yellow and one colourless, which were separated by fractional crystallization from the alcoholic solution. The more soluble substance crystallizes in yellow plates and melts at 143°. It is soluble in ether, alcohol, benzene and chloroform, but not in ligroin and water. The less soluble compound, which crystallizes in colourles needles, was found to possess all the properties of normal phenylphthalimide.

Being doubtful that the yellow substance might not be something else than von Gerichten's compound, it was analysed.

I. 0·2 grm. the substance gave 0·5860 grm. CO_2 and 0·009 grm. H_2O.

II. 0·6013 grm. the substance gave 0·0576 grm. nitrogen.

[1] Loc. cit.

Calc. for $C_6H_4\begin{cases}C{=}N{\cdot}C_6H_5\\ N{\cdot}C_6H_5.\\ CO\end{cases}$		Found. I.	Found. II.
Carbon	80·58	79·96	—
Hydrogen	4·07	5·00	—
Nitrogen	9·39	—	9·44
Oxygen	5·36	—	—

Moreover, the molecular weight of the substance was determined by the cryoscopic method, using benzene as a solvent, and the results were as follows:

Molecular depression for benzene = 50.

Expts.	Solvent.	Substance.	△	Mol. wt.
I.	20·73 grm.	0·0601 grm.	0·057°	261
II.	20·73 „	0·0835 „	0·076°	265
III.	20·73 „	0·1436 „	0·133°	262
IV.	20·73 „	0·2052 „	0·193°	260
V.	20·73 „	0·2688 „	0·250°	265

	Calc. for $C_{20}H_{14}N_2O$.	Found as mean.
Molecular weight	295	262

From the analytical results, as well as from the determination of the molecular weight, it is seen that the substance agrees in composition with that described by von Gerichten; but though it differs somewhat in its melting point from the latter substance, which is said to melt at 152–153°, both substances are no doubt identical, as all other properties agree so well.

5. *β-a-Phenylphthalimide*, $C_6H_4\begin{cases}C{=}N.C_6H_5\\ O.\\ CO\end{cases}$

The authors repeated the experiments of van der Meulen,[1] a

[1] Loc. cit.

number of times, exactly following the statements on his record, for the purpose of getting phthalophenylisoimide from phneylphthalamic acid by the action of acetyl chloride, but all their efforts ended, every time, in negative results, so that not a bit of it was isolated. From the pale-yellow crystalline substance formed as the direct reaction product, however, a compound consisting of almost colourless, fine needles was isolated by evaporating the etherial solution as quickly as possible. Its melting point was found to be 83–84°. Its analysis gave the following results:

I. 0·2 grm. the substance gave 0·5575 grm. CO_2 and 0·0769 grm. H_2O.
II. 0·5 grm. the substance gave 0·0309 grm. nitrogen.
III. 0·3 „ „ „ „ 0·0191 „ „

Calc. for $C_6H_4\langle{}^{C=N\cdot C_6H_5}_{CO}\rangle O$.		Found. I.	II.	III.
Carbon	75·33	76·02	—	—
Hydrogen	4·03	4·17	—	—
Nitrogen	6·27	—	6·19	6·39
Oxygen	14·34	—	—	—

It is seen from the analysis that the substance is isomeric with phenylphthalimide; but it is identical neither with Kuhara and Fukui's *a*-phenylphthalimide nor with van der Meulen's phthalophenylisoimide. It is readily soluble in ether, alcohol, and acetone. It changes to the normal phenylphthalimide with excessive readiness in its etherial solution, or upon being heated slightly by itself. By inference from such behaviour, the authors assume that it may be an unsymmetrical phenylphthalimide.

6. *The Second Compound Isomeric to Phenylphthalimide.*

By heating an alcoholic solution of the direct reaction product of phenylphthalamic acid and acetyl chloride, or the pale-yellow crystalline substance hereinbefore described, *β-a*-phenylphthal-

imide contained in it was found to change almost entirely to phenylphthalimide. The alcohol was distilled off from the solution and the residue was dissolved in ether. Then upon allowing the solution to evaporate, the less soluble normal phenylphthalimide crystallized out at first, and afterwards the more soluble new substance, crystallizable in amber-coloured rhombic prisms, separated out. The substance, purified by recrystallization, was observed to melt at 125–126°. It was analyzed and the results are as follows:

I.	0·23	grm.	the substance	gave	0·0141	grm.	nitrogen.
II.	0·46	„	„	„	0·0283	„	„
III.	0·30	„	„	„	0·0190	„	„

	Calc. for $C_{14}H_9NO_2$.	Found. I.	II.	III.
Nitrogen	6·27	6·15	6·15	6·30

The substance is readily soluble in alcohol and ether. Upon heating its acetic acid solution in a sealed tube at 120°, it changes to the normal phenylphthalimide, partly decomposing to aniline and phthalic acid. Crystals of it, when held on the loop of a platinum wire, and exposed to the flame of a burner burn with gentle detonation.

On the Solubility of Disodium Hydrogen Phosphate in Water.

By

Tsutomu Shiomi.

In the course of his studies on solubility determination by means of Pulfrich's refractometer, Prof. Y. Osaka[1] once noticed that the results of solubility determination of disodium hydrogen phosphate by Poggiale, Mulder, Neese, and others, diverge from one another. At his suggestion, I have undertaken the study of the same subject under his direction.

Experimental Methods.

A sufficient quantity of disodium hydrogen phosphate that had been twice re-crystallised, was introduced together with some water into a bottle, of about 50 c. c. capacity, which was previously well steamed. The bottle was closed with an indiarubber stopper which was tightly covered, as far as the neck of the bottle, with a sheet of oil-paper. It was then fixed on the stirrer of a thermostat and made to rotate under water for two or three days: after that the bottle was disconnected from the stirrer and allowed to stand in the thermostat for a while. When the solid particles had settled, the cover and the stopper were removed, the bottle was closed with a cork provided with a glass tube, bent twice at right angles, to connect the bottle with a short test tube B, previously weighed with an unbored cork; as shown in Fig. 1, and a portion of the clean solution in A was taken out into B by blowing at *b*.

The tube B, stoppered with the unbored cork, was weighed,

[1] These Memoirs, 1, 294.

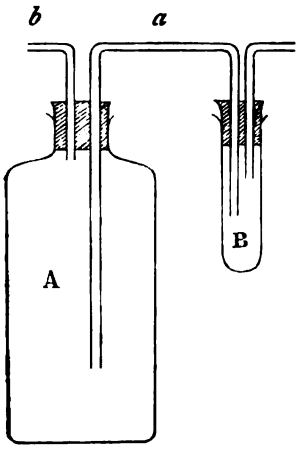


Fig. 1.

and its entire contents were transferred to a porcelain crucible, together with the wash-water. The liquid was evaporated by heating its surface and when dried, the residue was subjected to strong heat at the bottom until the weight became constant. From both the weight of the pyrophosphate thus formed and that of the solution taken, the solubility was calculated.

In each experiment, two bottles, such as have just been described, were made to rotate in the thermostat simultaneously: one of them was previously heated to a temperature about 10 degrees higher than that of the experiment, and allowed to deposit some of the solute on cooling to the temperature of the thermostat. Such method of procedure was employed at temperatures between 0·65° and 80°. At temperatures higher than 90°, the solutions were so highly concentrated that, when they were transferred from A to B, some of the solute was deposited in the connecting tube, *a*. In order to avoid such inconvenience, the test tube, B, was mantled with a somewhat larger tube, as shown in Fig. 2, and the bottle, test tube, and connecting tube were completely submerged in the liquid of the thermostat, prepared with calcium chloride solution.

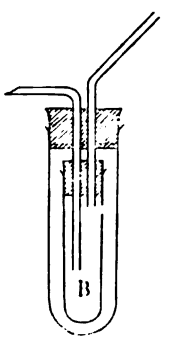


Fig. 2.

The thermometers used were standardised by means of a thermometer certified by Reichsanstalt. The temperature of the thermostat was constant within 0·1° during a single experiment but at temperatures higher than 90° it varied to the extent of 0·6.°

Results.

The experimental results are as follows:

Temperature.	Grms. PO_4HNa_2 in 100 grms. of water. Single determination.	Mean.
0·65	1·74	1·74
,,	,,	
,,	,,	
10·26	3·55	3·55
,,	3·54	
10·36	3·58	3·58
,,	3·59	
,,	3·58	
,,	3·58	
15·11	5·23	5·23
,,	5·22	
20·24	7·88	7·89
,,	7·90	
,,	7·89	
,,	7·89	
25·15	12·03	12·02
,,	12·01	
,,	12·01	
25·40	12·32	12·32
,,	12·34	
,,	12·31	
25·50	12·42	12·43
,,	12·41	
,,	12·47	
30·21	20·80	20·81
,,	20·76	
,,	20·88	

Temperature.	Grms. PO_4HNa_2 in 100 grms. of water. Single determination.	Mean.
30·26	21·60	
"	21·62	
"	21·56	
"	21·55	
"	21·56	... ... 21·59
"	21·61	
"	21·60	
"	21·59	
"	21·59	
30·76	23·42	
"	23·40	... ... 23·41
"	23·41	
33·04	30·88	... ... 30·88
"	30·88	
33·14	31·39	... ... 31·38
"	31·37	
36·27	45·36	
"	45·35	
"	45·34	
"	45·38	
"	45·39	... ... 45·37
"	45·36	
"	45·41	
"	45·36	
"	45·35	
37·27	47·56	
"	47·48	
"	47·46	
"	47·53	... ... 47·51
"	47·56	
"	47·48	
"	47·49	
"	47·56	

Temperature.	Grms. PO_4HNa_2 in 100 grms. of water. Single determination.	Mean.
40·29	54·95	54·88
,,	54·86	
,,	54·95	
,,	54·83	
,,	54·85	
,,	54·88	
45·14	68·67	68·64
,,	68·68	
,,	68·61	
,,	68·58	
47·23	76·60	76·58
,,	76·55	
48·23	80·03	80·03
48·33	80·12	80·15
,,	80·17	
50·22	80·40	80·35
,,	80·34	
,,	80·32	
,,	80·36	
55·17	81·37	81·40
,,	81·43	
55·27	81·61	81·64
,,	81·66	
60·23	83·01	83·00
,,	83·02	
,,	82·98	
70·26	88·10	88·11
,,	88·17	
,,	88·07	

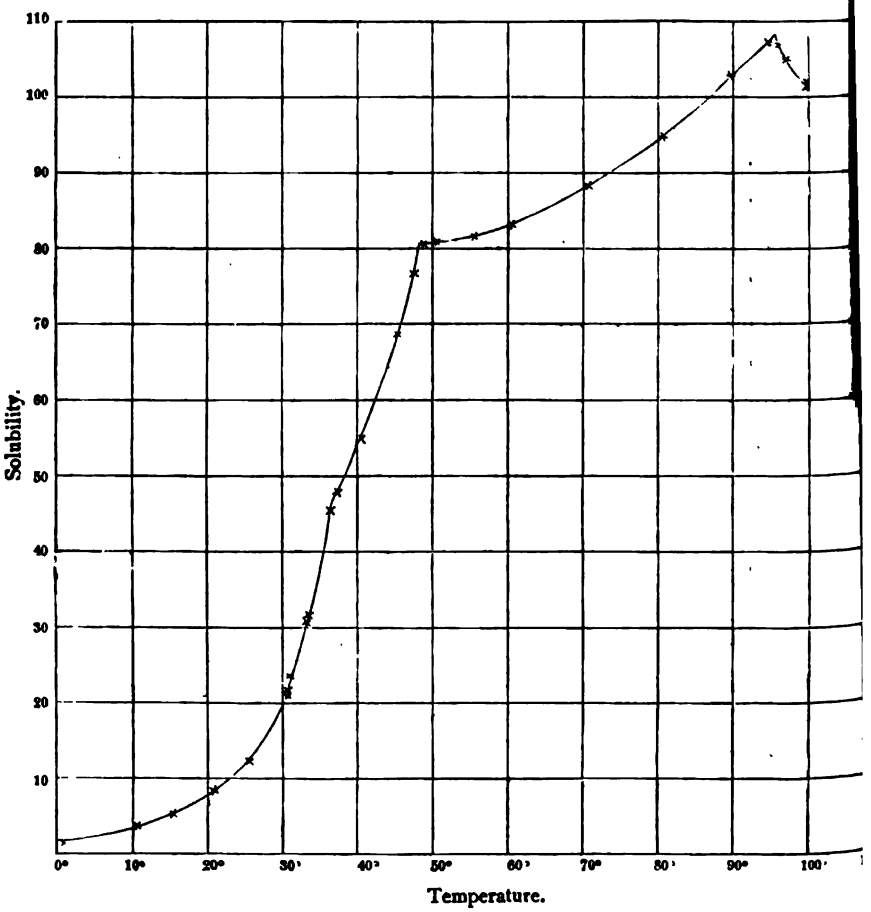
Temperature.	Grms. PO_4HNa_2 in 100 grms of water. Single determination.	Mean.
80·39	94·74	
"	94·83	... ... 94·78
"	94·76	
89·74	102·85	
"	102·89	... ... 102·87
94·75	107·31	
"	107·37	... ... 107·34
"	107·34	
95·86	107·08	
"	107·09	... ... 107·09
96·86	104·94	
"	105·01	... ... 104·98
99·57	101·25	
"	101·22	... ... 101·21
"	101·16	
99·77	102·12	
"	102·16	... ... 102·15
"	102·16	

By taking the temperatures for abscissae, and the grams of disodium hydrygen phosphate, calculated as anhydrous, contained in 100 grams of water, for ordinates, we are able to plot the the solubility curve as shown in Fig. 3. On looking at the curve, we notice three breaks, at 36·45°, 48·0°, and 95·2° respectively. The point corresponding to the first break has already been observed by several investigators, and is nothing but the transition point of the dodecahydrate to the heptahydrate: such point, as determined by Person,[1] Tilden,[2] and Baur[3] is

[1] Ann chim. phys. (3) **27**, 258 (1849).
[2] Journ. Chem. Soc. **45**, 268 (1884).
[3] Zeitschr. f. physik. Chem. **18**, 180 (1895).

shown to be 36·4°, 35·0°, and 36·6° respectively. As to the other breaks, nothing is mentioned in the literature. In Landolt-Bernstein-Meyerhoffer's Tables[1] the composition of the solid phase

Fig. 3.



in the solubility determination of the salt at 52·7° and higher temperatures, is not given, and is marked only with "?," while in

[1] p. 558.

Seidell's "Solubility of Inorganic and Organic Substances,"[1] this salt is stated, even up to 100°, to be dodecahydrate. According to Lescoeur[2] the hydrate of disodium hydrogen phosphate are nothing but the dodecahydrate and heptahydrate. Muller-Ergbach[3] who determined the vapour tension of the hydrated salt at several temperatures up to 61·8°, has never noticed the existence of any other hydrate. Now, from the solubility determination so far reported, it is evident that at 48·0° and 95·2° the solid phase undergoes some change. It is probably due to the formation of a lower hydrate and of the anhydrous salt at respective temperatures.[4]

November, 1908.

[1] p. 310.

[2] Ann. chim. phys. (6) **21**, 551 (1890).

[3] Ber. d. chem. Gesell. **20**, 137 (1887).

[4] Studies on the solid phases and on the transition points, are now in progress in this laboratory, and the solid phases which happen to exist at 48·0° and 95·2° seem to consist of the dihydrate and of the anhydrous salt respectively.

On the Dirichlet's Principle.

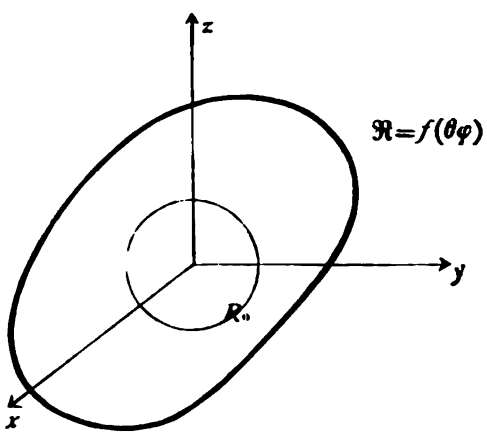
By

Masamichi Kimura.

Let $\mathfrak{R}=f(\theta, \varphi)$ be the equation of a closed surface, in which $f(\theta, \varphi)$ is one valued and continuous with respect to θ and φ, and satisfies the following relations for the fixed values of k_1, and k_2,

$$o<k_1<|f(\theta, \varphi)|<k_2,$$

whatever the values of θ and φ may be.



Describe a sphere of a finite radius R_0, which is less than k_1, the centre being at the origin. Define a point (ξ, η, ζ) by the relations.

$$\left.\begin{aligned} x&=\frac{\mathfrak{R}}{R_0}\xi \\ y&=\frac{\mathfrak{R}}{R_0}\eta \\ z&=\frac{\mathfrak{R}}{R_0}\zeta \end{aligned}\right\}, \quad \text{or} \quad \left.\begin{aligned} \xi&=\frac{R_0}{\mathfrak{R}}x \\ \eta&=\frac{R_0}{\mathfrak{R}}y \\ \zeta&=\frac{R_0}{\mathfrak{R}}z \end{aligned}\right\} \cdots \cdots \cdots (1),$$

where (x, y, z) are the coordinates of the point in the old system, and (ξ, η, ζ) those in the new system.

Again, let (r, θ, φ), $(r_1, \theta_1, \varphi_1)$ be the polar coordinates of the same point in the old and the new systems, then we have

$$\theta=\theta_1, \qquad \varphi=\varphi_1,$$

$$\text{and} \quad r_1=\frac{R_0}{\mathfrak{R}}r.$$

Denote the transformation of a point defined by (1) by the notation S. Then applying S to a point P, it comes to P' whose position is obtained by the simple geometrical construction represented by

$$r_1=\frac{R_0}{\mathfrak{R}}r \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (2).$$

This transformation is represented by the notation

$$P.S=P' \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (3).$$

If we denote the inverse transformation of S by S^{-1}, we have evidently

$$S.S^{-1}=1,$$

where 1 denotes the identical transformation.

Operating S^{-1} upon the both sides of (3), we have

$$P=P'.S^{-1} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (4).$$

We see from (3) and (4), that if the surfaces of the reference R_0 and $\mathfrak{R}$ are given, a point P is transformed into a certain fixed point P' by the transformation S, and the one and only one point P' corresponds to P with respect to S.

If the point P lies on the surface of $\mathfrak{R}$, its corresponding point is the intersection-point of the radius vector of P with the surface of the reference sphere. All the points external to the surface $\mathfrak{R}$ are transformed to the points external to the surface of the sphere, while all the points internal to $\mathfrak{R}$ are transformed to the internal points of the sphere.

Let us now consider a function $F(x, y, z)$ of a point $P(x, y, z)$. Applying the transformation S to $F(x, y, z)$ it becomes the function of the corresponding point $P'(\xi, \eta, \zeta)$ and this is expressed by

$$F(x, y, z).S=F_1(\xi, \eta, \zeta) \ldots \quad \ldots \quad \ldots \quad (5).$$

if F is a continuous function of x, y and z, then F_1 is also the continuous function of ξ, η and ζ.

The space enclosed by $\mathfrak{R}=f(\theta, \varphi)$ is also transformed to the space within the sphere by S, and this is denoted by

$$\tau . S = \tau' \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (6),$$

where τ and τ' are the volumes of $\mathfrak{R}=f(\theta, \varphi)$ and the sphere respectively.

The inverse of (5) and (6) are also true.

From these relations, we see that the transformations S and S^{-1} give the one and only one corresponding relation.

With these preliminaries, we shall proceed to the discussion of the Dirichlet's Principle.

Let τ be the space in which the potential function is sought, and let $F(r, \theta, \varphi)$ be one valued and continuous function on the boundary of τ, i. e. on the surface $\mathfrak{R}=f(\theta, \varphi)$.

If we apply the transformation denoted by S to τ and F, we have

$$\left.\begin{array}{l} \tau . S = \tau' \\ F . S = F_1 \end{array}\right\} \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (7).$$

The boundary condition is thus reduced to F_1, which is one valued and continuous function on the surface of the sphere, provided that F is so on the surface $\mathfrak{R}=f(\theta, \varphi)$. The space in which V is required, is transformed to the space within the sphere of the radius R_0, and therefore the Dirichlet's Principle for the surface $\mathfrak{R}=f(\theta, \varphi)$ is equivalent to the new problem:

It is required to find the one valued and continuous function whose first derivatives with respect to x, y and z are also continuous, and its second derivatives are finite throughout the space within the sphere (R_0) and satisfy the transformed Laplace's equation with the corresponding boundary condition.

This is the principle which leads to my solution of Dirichlet's Principle for a closed surface $\mathfrak{R}=f(\theta, \varphi)$.

EXISTENCE-THEOREM.

Since F_1 satisfies the conditions for the expansion in the series of the spherical harmonics, we have

$$\left.\begin{aligned} F_1 &= \sum_0^\infty Y_m(\mu, \varphi) \\ \text{or} \quad F &= \sum_0^\infty Y_m(\mu, \varphi)\, S^{-1} \end{aligned}\right\} \quad \dots \quad \dots \quad \dots \quad (8),$$

where

$$Y_m(\mu, \varphi) = [A_{0,m} P_m(\mu) + \sum_{n=1}^{m} (A_{n,m} \cos n\varphi + B_{n,m} \sin n\varphi) P_m^n(\mu)] \dots \quad (9),$$

and

$$\left.\begin{aligned} A_{0,m} &= \frac{2m+1}{4\pi} \int_0^{2\pi} d\varphi \int_{-1}^{+1} F_1(\mu,\varphi) P_m(\mu)\, d\mu. \\ A_{n,m} &= \frac{2m+1}{2\pi} \frac{(m-n)!}{(m+n)!} \int_0^{2\pi} d\varphi \int_{-1}^{+1} F_1(\mu,\varphi) P_m^n(\mu) \cos(n\varphi)\, d\mu, \\ B_{n,m} &= \frac{2m+1}{2\pi} \frac{(m-n)!}{(m+n)!} \int_0^{2\pi} d\varphi \int_{-1}^{-1} F_1(\mu,\varphi) P_m^n(\mu) \sin(n\varphi)\, d\mu. \end{aligned}\right\} \quad (10).$$

If we apply the transformation S to Laplace's equation in the spherical coordinates, it takes the form

$$r_1 \frac{\partial^2}{\partial r_1^2}(r_1 V) - r_1 \frac{\partial V}{\partial r_1} + \frac{1}{\sin\theta} \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial V}{\partial\theta}\right) + \frac{1}{\sin^2\theta} \frac{\partial^2 V}{\partial\varphi^2} = 0 \quad \dots \quad \dots \quad \dots \quad (11).$$

Assuming that

$$V = R.\ \Theta.\ \Phi \dots \quad \dots \quad \dots \quad \dots \quad (12),$$

where R, Θ and Φ are function of r, θ and φ respectively, we have

$$r_1 \frac{d^2}{dr_1^2}(r_1 R)\, \Theta\, \Phi + \frac{1}{\sin\theta} \frac{d}{d\theta}\left\{\sin\theta \frac{d\Theta}{d\theta}\right\} R\Phi + \frac{R\Theta}{\sin^2\theta} \frac{d^2\Phi}{d\varphi^2} - r_1 \Theta\Phi \frac{dR}{dr_1} = 0,$$

or
$$\frac{r_1\frac{d^2}{dr_1^2}(r_1R)-r_1\frac{dR}{dr_1}}{R}+\frac{1}{\sin\theta}\cdot\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)$$
$$+\frac{1}{\sin^2\theta.\Phi}\frac{d^2\Phi}{d\varphi^2}=0. \quad \dots \quad (13).$$

This equation shows that

$$\frac{r_1\frac{d^2}{dr_1^2}(r_1R)-r_1\frac{dR}{dr_1}}{R} \quad \text{and} \quad \frac{\frac{d^2\Phi}{d\varphi^2}}{\Phi}$$

are constant, and therefore, putting

$$\frac{r_1\frac{d^2}{dr_1^2}(r_1R)-r_1\frac{dR}{dr_1}}{R}=m(m+1) \quad \dots \quad \dots \quad (14),$$

and

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2}=-n^2 \dots \quad \dots \quad \dots \quad \dots \quad (15),$$

we have

$$R=r_1^{\pm\sqrt{m(m+1)}} \quad \dots \quad \dots \quad \dots \quad \dots \quad (16),$$

$$\Phi=\sin n\varphi, \text{ or } \cos n\varphi \dots \quad \dots \quad \dots \quad (17).$$

Substituting (14) and (15) in (13), we have

$$m(m+1)+\frac{1}{\sin\theta.\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)-\frac{n^2}{\sin^2\theta}=0 \quad \dots \quad \dots \quad (18).$$

For a positive integral value of n, this equation is satisfied by the associated Legendre's function of the order n and the degree m, i. e.

$$\Theta=P_m^n(\cos\theta) \quad \dots \quad \dots \quad \dots \quad \dots \quad (19).$$

Hence

$$V.S=\sum_0^\infty Y_m(\mu,\varphi)\left(\frac{r_1}{R_0}\right)^{\sqrt{m(m+1)}} \quad \dots \quad \dots \quad (20),$$

is a solution of (11) and it takes the value F_1 on the surface of the sphere, and within which it satisfies the conditions of the problem.

Applying the inverse transformation S^{-1} to (20), we have

$$V=\sum_{0}^{\infty}\left\{Y_m(\mu,\varphi)\left(\frac{r_1}{R_0}\right)^{\sqrt{m(m+1)}}\right\}.S^{-1} \quad \ldots \quad \ldots \quad (21).$$

This is a solution of Laplace's equation satisfying the conditions of the problem. For V given in (21) is one valued and continuous function and its first derivatives are also continuous at every point in τ, and the second derivatives are finite throughout the space τ, and since $V.S$ satisfies the transformed Laplace's equation V satisfies Laplace's equation and, lastly, it takes the value

$$V=F=\sum_{0}^{\infty}Y_m(\mu,\varphi).S^{-1}$$

on the surface $r=\mathfrak{R}$, because

$$\frac{r_1}{R_0}=\frac{r}{\mathfrak{R}}.$$

Thus a solution satisfying the conditions of the problem exists.

In the like manner

$$V=\sum_{0}^{\infty}\left\{Y_m(\mu,\varphi)\left(\frac{r}{\mathfrak{R}}\right)^{-\sqrt{m(m+1)}}\right\}.S^{-1} \quad \ldots \quad (22),$$

is a solution of Laplace's equation satisfying the conditions of the problem in the space external to τ and takes the given boundary value on the surface $\mathfrak{R}$.

Unique-Solution.

Suppose V and V' are two solutions satisfying the conditions of the problem. Then if we put

$$W=V-V',$$

W has the properties of the potential function, and therefore it is continuous at every point within (or without) τ, and it vanishes at every point on the surface $\mathfrak{R}=f(\theta,\varphi)$ (or and at infinity). If W were different from zero at the all points in τ (or in the space external to τ), there must be at least one point where W takes an extreme value. This is impossible, and therefore

$$W=0, \quad \text{or} \quad V=V',$$

at every point in the space τ, (or in the space external to τ).

Thus the solution is unique.

Motion of a Negative Electric Charge in the Field due to an Electric Doublet.

By

Masamichi Kimura.

The problem of motion under two centres of force was first investigated by Euler. Lagrange, Liouville, Serret and others had extended the results. We shall now apply the results obtained by them to a negative electric charge placed in the field due to an electric doublet. Since the field is symmetrical about the axis of the doublet, it is sufficient to consider the motion in a plane passing through the axis, when the initial velocity is zero, or when its direction cuts the axis of the doublet, produced if necessary.

Taking two points, $y=o$, $x=\pm h$, let us consider two confocal conics whose foci are $y=o$, $x=\pm h$. Let the semi major axes be μ and ν, and r_1, r_2 the distances of a point P from the foci whose elliptic coordinates are (μ, ν), then we have

$$r_1=\mu-\nu, \quad r_2=\mu+\nu.$$

If the central forces tending to the foci be respectively $\frac{H_1}{r_1^2}$ and $\frac{H_2}{r_2^2}$, the integrals of the equations of motion are given by

$$\frac{d\mu}{\sqrt{(\mu^2-h^2)(C\mu^2+K_1\mu+A)}}=\frac{d\nu}{\sqrt{(\nu^2-h^2)(C\nu^2-K_2\nu+A)}}=\frac{\sqrt{2}\,dt}{\mu^2-\nu^2} \quad (1),$$

where

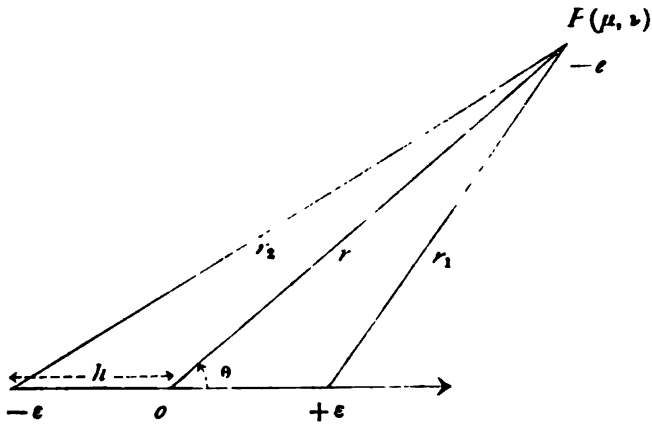
$$K_1=H_1+H_2, \quad \text{and} \quad K_2=H_1-H_2,$$

A and C being the integration constants.

Now consider an electric charge $+\varepsilon$ at $x=h, y=o$, and another charge $-\varepsilon$ at $x=-h$, $y=o$, then the electric forces due to the doublet at the charge $-e$ placed at the point $P(\mu, \nu)$ are

$$-\frac{\varepsilon e}{r_1^2}, \text{ and } +\frac{\varepsilon e}{r_2^2},$$

so that $$K_1=0, \text{ and } K_2=-2\varepsilon e.$$



But at a sufficiently great distance from the origin O

$$2\mu=r_1+r_2=2r,$$
$$2\nu=r_2-r_1=2h\cos\theta,$$

i. e.

$$\mu=r,$$
$$\nu=h\cos\theta,$$

and therefore

$$d\mu=dr,$$
$$d\nu=-h\sin\theta\, d\theta.$$

At a great distance from the origin, we may neglect h^2 in comparison with r^2, and $Ch^2\cos^2\theta$ with $2\varepsilon e h\cos\theta+A$, because $2h\varepsilon=\omega$ is the moment of the doublet and therefore finite.

Introducing the above relations in (1), we obtain

$$\frac{dr}{r\sqrt{(Cr^2+A)}}=\frac{-d(\theta+\pi)}{\sqrt{\omega e}\sqrt{\cos(\theta+\pi)-\frac{A}{\omega e}}}=\frac{\sqrt{2}\,dt}{r^2} \quad \ldots \quad \ldots (2).$$

The expression $\sqrt{\cos(\theta+\pi)-\frac{A}{\omega e}}$ is real only when

$$\cos(\theta+\pi)>\frac{A}{\omega e},$$

and therefore for the possible motion $\frac{A}{\omega e}$ must be less than unity, so that we may put

$$\frac{A}{\omega e}=\cos a.$$

Substituting this value in (2), the above relations become

$$\frac{dr}{r\sqrt{Cr^2+A}}=\frac{-d\varphi}{\sqrt{\omega e}\sqrt{\cos\varphi-\cos a}}=\frac{\sqrt{2}\,dt}{r^2},$$

where $$\varphi=\theta+\pi.$$

Now,

$$\cos\varphi-\cos a=2\left(\sin^2\frac{a}{2}-\sin^2\frac{\varphi}{2}\right).$$

If we put

$$\sin\frac{\varphi}{2}=\sin\frac{a}{2}\sin\psi,$$

then

$$d\varphi=\frac{2\sin\frac{a}{2}\cos\psi}{\cos\frac{\psi}{2}}d\psi,$$

$$=\frac{2\sin\frac{a}{2}\cos\psi}{\sqrt{1-\sin^2\frac{a}{2}\sin^2\psi}}d\psi,$$

and therefore

$$\sqrt{\sin^2\frac{\alpha}{2}-\sin^2\frac{\varphi}{2}}=\sqrt{\sin^2\frac{\alpha}{2}(1-\sin^2\psi)}$$

$$=\sin\frac{\alpha}{2}\cos\psi.$$

Hence,

$$\frac{d\varphi}{\sqrt{\cos\varphi-\cos\alpha}}=\frac{2\sin\frac{\alpha}{2}\cos\psi d\psi}{\sqrt{1-\sin^2\frac{\alpha}{2}\sin^2\psi}\ \sqrt{2}\sin\frac{\alpha}{2}\cos\psi},$$

$$=\frac{\sqrt{2}\,d\psi}{\sqrt{1-\sin^2\frac{\alpha}{2}\sin\psi}},$$

so that

$$\frac{-d\varphi}{\sqrt{\omega e}\sqrt{\cos\varphi-\cos\alpha}}=-\sqrt{\frac{2}{\omega e}}\ \frac{d\psi}{\sqrt{1-\sin^2\frac{\alpha}{2}\sin^2\psi}}.$$

Thus we have

$$\frac{dr}{r\sqrt{Cr^2+A}}=-\sqrt{\frac{2}{\omega e}}\ \frac{d\psi}{\sqrt{1-\sin^2\frac{\alpha}{2}\sin^2\psi}}=\frac{\sqrt{2}\,dt}{r^2}\quad\ldots\quad\ldots\ (3),$$

where

$$\sin\psi=\frac{\sin\frac{\theta+\pi}{2}}{\sin\frac{\alpha}{2}}.$$

From (3) we have

$$\sqrt{2}\,dt=\frac{rdr}{\sqrt{Cr^2+A}},$$

or

$$r^2=C(\sqrt{2}\,t-B)^2-\frac{A}{C}\quad\ldots\quad\ldots\quad\ldots\quad\ldots\ (4),$$

B being the integration constant.

Eliminating r from (3) and (4), we have

$$-\frac{1}{\sqrt{\omega e}}\frac{d\psi}{\sqrt{1-\sin^2\frac{a}{2}\sin^2\psi}}=\frac{dt}{C(\sqrt{2}\,t-B)^2-\frac{A}{C}}.$$

We shall now distinguish between the following three cases:

(i) $A>0$. In this case, the integral of the equation becomes

$$-\frac{1}{\sqrt{\omega e}}F(\psi, a)=\frac{1}{2\sqrt{2A}}\log\frac{\sqrt{2}\,t-B-\frac{\sqrt{A}}{C}}{\sqrt{2}\,t-B+\frac{\sqrt{A}}{C}}+D_1.$$

(ii) $A=0$. In this case

$$-\frac{1}{\sqrt{\omega e}}F(\psi, a)=-\frac{1}{\sqrt{2}C(\sqrt{2}\,t-B)}+D_2.$$

(iii) $A<0$. In this case

$$-\frac{1}{\sqrt{\omega e}}F(\psi, a)=\frac{1}{\sqrt{-2A}}\tan^{-1}\frac{C(\sqrt{2}\,t-B)}{\sqrt{-A}}+D_3.$$

In the above, D_1, D_2, and D_3 are the integration constants.

If we define T_1, T_2, and T_3 by the equations:

$$\left.\begin{aligned}
T_1&=-\frac{\sqrt{\omega e}}{2\sqrt{2A}}\cdot\log\frac{\sqrt{2}\,t-B-\frac{\sqrt{A}}{C}}{\sqrt{2}\,t-B+\frac{\sqrt{A}}{C}}+D_1\\
T_2&=\frac{\sqrt{\omega e}}{\sqrt{2}C}\cdot\frac{1}{\sqrt{2}\,t-B}+D_2\\
T_3&=-\frac{\sqrt{\omega e}}{\sqrt{-2A}}\tan^{-1}\frac{C(\sqrt{2}t-B)}{\sqrt{-A}}+D_3
\end{aligned}\right\}\quad\cdots\quad\cdots\quad(5),$$

ψ is given by the equations,

$$\psi = am\ T_n, \qquad n = 1,\ 2,\ 3.$$

Therefore

$$\sin\psi = \mathrm{sn}\ T_n,$$

or

$$\cos\frac{\theta}{2} = \sin\frac{\alpha}{2}\mathrm{sn}\ T_n \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (6).$$

Thus the equations (4) and (6) with (5) give the solution of the problem.

We now proceed to study the nature of the solutions corresponding to the cases described above.

Case I. $\alpha = o$, i. e. $\cos\alpha = 1$, and $A = \omega e$.

In this case $\sqrt{\cos(\theta+\pi) - \cos\alpha}$ is real only when

$$\theta + \pi = o, \text{ or } 2\pi,$$

i. e.

$$\theta = \pm\pi.$$

Therefore the equations of the path are given by

$$r^2 = C(\sqrt{2}\,t - B)^2 - \frac{\omega e}{C},$$

$$\theta = \pm\pi.$$

Thus the charge moves in a straight line $\theta = \pm\pi$.
The velocity of the charge is

$$\frac{dr}{dt} = \frac{\sqrt{2}}{r}\sqrt{Cr^2 + A} = \sqrt{2}\sqrt{C + \frac{A}{r^2}}$$

$$\doteqdot \sqrt{2C},$$

if r is sufficiently great.

And

$$r\frac{d\theta}{dt} = 0.$$

The charge therefore moves in the axis of the doublet with the velocity

$$\sqrt{2}\sqrt{C+\frac{A}{r^2}}.$$

Case II. $\quad 0<\alpha<\pi/2,$

i. e. $\quad \omega e>A>0.$

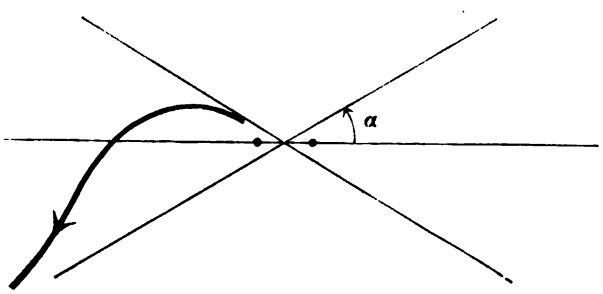
In this case $\sqrt{\cos(\theta+\pi)-\cos\alpha}$ is real when

$$\pi-\alpha<\theta<\pi+\alpha,$$

and the equations of the path are given by

$$r^2=C(\sqrt{2}\,t-B)^2-\frac{A}{C},$$

$$\cos\frac{\theta}{2}=\sin\frac{\alpha}{2}\,\mathrm{sn}\,T_1.$$



The components of the velocity are

$$\frac{dr}{dt}=\sqrt{2}\sqrt{C+\frac{A}{r^2}},$$

$$r\frac{d\theta}{dt}=\sqrt{2}\frac{\sqrt{\omega e\cos(\theta+\pi)-A}}{r}$$

$$=\left\{\frac{4\,\omega e\left(\sin^2\frac{\alpha}{2}\mathrm{sn}^2T_1-\cos^2\frac{\alpha}{2}\right)}{C(\sqrt{2}\,t-B)^2-\frac{A}{C}}\right\}^{\frac{1}{2}}.$$

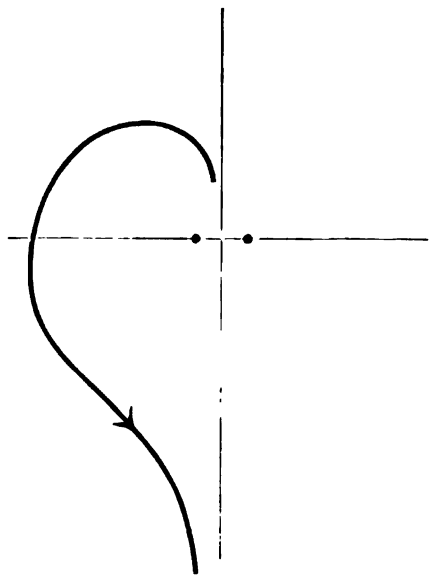
From this we see that $\frac{d\theta}{dt}$ is always positive, and does not change its sign, and consequently there is no retrograde motion in the direction of θ.

Case III. $\alpha=\pi/2$,

i. e. $\cos\alpha=0$, $A=0$.

In this case the path is real when

$$\pi/2<\theta<3/2\pi,$$



and the equations of the path are

$$r^2=C(\sqrt{2}\,t-B)^2,$$

$$\cos\frac{\theta}{2}=\frac{1}{\sqrt{2}}\operatorname{sn} T_2,$$

the component velocities being

$$\frac{dr}{dt}=\sqrt{2}\sqrt{C+\frac{A}{r^2}},$$

$$r\frac{d\theta}{dt}=\sqrt{2}\,\frac{\sqrt{\omega e\cos(\theta+\pi)}}{r},$$

$$=\sqrt{\frac{2\omega e}{C}}\;\frac{\operatorname{cn} T_2}{\sqrt{2}\,t-B}.$$

The motion is also unidirectional with respect to θ.

Case IV. $\frac{\pi}{2}<\alpha<\pi$,

i. e. $0>A>-\omega e$.

In this case the path is real when

$$\pi-\alpha<\theta<\pi+\alpha,$$

and the equations of orbit become

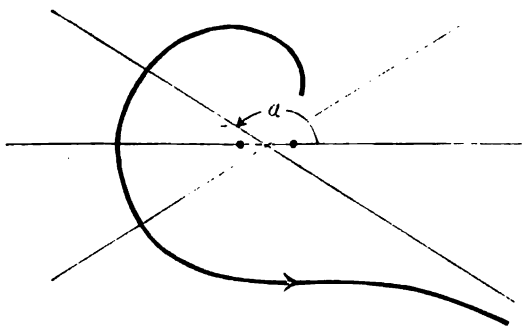
$$r^2=C(\sqrt{2}\,t-B)^2-\frac{A}{C},$$

$$\cos\frac{\theta}{2}=\sin\frac{\alpha}{2}\operatorname{sn} T_3.$$

The component-velocities are

$$\frac{dr}{dt}=\sqrt{2}\sqrt{C+\frac{A}{r^2}},$$

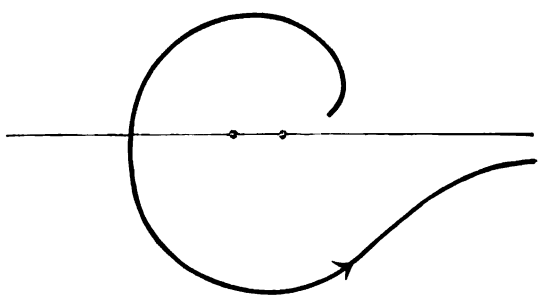
$$r\frac{d\theta}{dt}=\left\{\frac{4\,\omega e\left(\sin^2\frac{\alpha}{2}\,\mathrm{sn}^2 T_3-\cos^2\frac{\alpha}{2}\right)}{C(\sqrt{2}\,t-B)^2-\frac{A}{C}}\right\}^{\frac{1}{2}},$$



and therefore there is no retrograde motion in the direction of θ.

Case V. $\alpha=\pi$,

i. e. $A=-\omega e$, $\sin\frac{\alpha}{2}=1$.



In this case the path is real for such a value of θ as

$$0<\theta<2\pi,$$

and the equations of the orbit become

$$r^2 = C(\sqrt{2}\,t - B)^2 + \frac{\omega e}{C},$$

$$\cos\frac{\theta}{2} = \tanh T_3,$$

$$= \frac{e^{T_3} + e^{-T_3}}{e^{T_3} - e^{-T_3}}.$$

The component velocities are given by

$$\frac{dr}{dt} = \sqrt{2}\sqrt{C + \frac{A}{r^2}},$$

$$r\frac{d\theta}{dt} = 2.\frac{\sqrt{\omega e}\,\text{sech.}\,T_3}{\sqrt{C(\sqrt{2}\,t - B)^2 + \frac{\omega e}{C}}}.$$

Consequently there is no retrograde motion in the direction of θ.

Thus in all cases, a negative point charge, if it is placed at a sufficiently great distance from the electric doublet, goes away to infinity with a constant radical velocity, as indicated by the foregoing figures.

Amine Salts of Phthalamic, Phenylphthalamic, and Phenylsuccinamic Acids.

By

Shigeru Komatsu.

Some years ago, Remsen and Kohler[1] obtained the aniline salt of orthosulphanilidobenzoic acid by the interaction of the acid and aniline, and Sohn[2] also prepared the aniline benzanilidosulphonate, and the toluidine benztoluidosulphonate, by similar method.

Tingle and Lovelace[3] once predicted the possibility of the existence of the aniline phenylphthalate, but actually could obtain nothing but phenylphthalimide by the action of aniline upon phenylphthalamic acid, though it ought to form an aniline salt like orthosulphanilidobenzoic, benzanilidosulphonic and benztoluidosulphonic acids. Such discrepancies as Remsen, Kohler and Sohn's, to get the salts, on one hand, and Tingle and Lovelace's unsuccessful effort, on the other, may have depended upon the stability of those salts against water and other agents.

It was actually shown by Sohn[4] that the toluidine salt of benztoluidosulphonic acid is stable toward boiling water. Now, it has occurred to the author that if phenylphthalamic acid, which must be a much weaker acid than benztoluidosulphonic acid and whose amine salts would therefore, undergo hydrolysis or decomposition readily by water, alkali or acid, simply acts upon amines,

[1] Amer. Chem. Journ, **17**, 343.
[2] Ibid. **20**, 273.
[3] Ibid. **38**, 644.
[4] Ibid. **20**, 275.

especially in absolute-alcoholic solution, its amine salts should be formed and remain undecomposed.

In carriying out experiments, phenylphthalamic acid and amines were mixed together, each having been dissolved in absolute alcohol, and the mixture was kept at ordinary temperature. After standing for a few days, the amine salts were found to have separated in a crystalline state. The salts thus formed are unstable toward water, alkali, or acid, easily decomposing into phenylphthalimide and amines.

Upon conducting similar experiments with phthalamic and phenylsuccinamic acids under the same conditions as in the case of phenylphthalamic acid, there were obtained the corresponding salts of the respective acids, which behave analogously to the amine salts of phenylphthalamic acid.

EXPERIMENTS.

1. *Aniline Phenylphthalamate*, $C_6H_4\begin{cases}CONHC_6H_6\\COONH_3C_6H_5\end{cases}$.

In preparation, anilme (1 mol.) was added to an alcoholic solution of phenylphthalamic acid (1 mol.), prepared by the method suggested by Laurent and Gerhardt.[1] After the mixed solution had been kept at ordinary temperature for a few days, white hexagonal crystals of aniline phenylphthalamate separated out. The salt is soluble in alcohol but not in ether or chloroform: the melting-point was found to be 124°–125°. The substance, after having been dried over sulphuric acid, was analysed, and the results are as follows:

0·37 grm. the substance gave 0·032 grm. nitrogen.

	Calc. for $C_6H_4\begin{cases}CONHC_6H_5\\COONH_3C_6H_5\end{cases}$	Found.
Nitrogen	8·38	8·62

[1] Ann. d. Chem., **68**, 34.

It was noticed that the substance decomposes into phenylphthalamide and aniline, when heated in alcoholic or aqueous solution, or when treated with alkali or acid.

In order to ascertain the exact nature of the salt by determining the quantity of aniline set free by its hydrolysis through the influence of mineral acid, the author took a definite quantity of the salt and treated it with an excess of hydrochloric acid. The acid solution was evaporated over a water bath, the aniline salt formed converted into the platinum double salt, and analysed.

0·3 grm. the salt gave 0·085 grm. platinum on ignition.

	Calc. for $C_6H_4\begin{cases}CONHC_6H_5\\COONH_3C_6H_5\end{cases}$	Found.
$C_6H_5NH_2$	27·84	27·13

2. *Methylamine Phenylphthalamate*, $C_6H_4\begin{cases}CONHC_6H_5\\COONH_3CH_3\end{cases}$.

After allowing the mixture of methylamine and the acid, both dissolved in absolute alcohol, to stand, colourless needle-shaped crystals of methylamine phenylphthalamate were obtained. The salt was found to be soluble in water or alcohol, but not in ether: the melting point was noted at 115°. Upon treating the crystals with mineral acid or alkali, or by heating them with water, they were observed to decompose into methylamine and phenylphthalimide. The salt, dried over sulphuric acid, was analysed:

0·33 grm. the substance gave, 0·0321 grm. nitrogen.

	Calc. for $C_6H_4\begin{cases}CONHC_6H_5\\COONH_3CH_3\end{cases}$	Found.
Nitrogen	9·76	9·75

Methylamine hydrochloride formed from the salt by the decom-

position with hydrochloric acid, was analysed, after converting into platinum double salt.

0·2 grm. the substance gave 0·0675 grm. platinum on ignition.

	Calc. for $C_6H_4\begin{cases}CONHC_6H_5\\COONH_3CH_3.\end{cases}$	Found.
CH_3NH_2	34·09	33·75

3. *β-Naphthylamine Phenylphthalamate*, $C_6H_4\begin{cases}CONHC_6H_5\\COONH_3C_{10}H_7.\end{cases}$

The salt was prepared as a white crystalline precipitate from β-naphthylamine and phenylphthalamic acid: it is soluble in alcohol, but not in ether: its melting point was found to be 170°–173°.

The behaviour of the salt is, in all respects, analogous to that of the phenylphthalamates already described.

β-Naphthylamine contained in the salt was determined as the platinum double chloride:

0·376 grm. the salt gave, 0·1467 grm. naphthylamine.

	Calc. for $C_6H_4\begin{cases}CONHC_6H_5\\COONH_3C_{10}H_7.\end{cases}$	Found.
$C_{10}H_7NH_2$	39·56	39 04

4. *Benzylamine Phenylphthalamate*, $C_6H_4\begin{cases}CONHC_6H_5\\COONH_3CH_2C_6H_5.\end{cases}$

Benzylamine phenylphthalamate prepared from benzylamine and the acid in an analogous way, consists of colourless needle-shaped crystals, and is soluble in alcohol but not in ether or benzene: it melts at 138°–159°. Its behaviour is analogous to that of other phenylphthalamates: it was analysed and gave the following results:

0·5 grm. the substance gave, 0·041 grm. nitrogen.

	Calc. for $C_6H_4\begin{cases}CONHC_6H_5\\COONH_3CH_2C_6H_5.\end{cases}$	Found.
Nitrogen	8·05	8·09

Benzylamine hydrochloride formed from the original salt was analysed as its double salt of platinum, and gave the following result:

0·4 grm. the salt gave, 0·1248 grm. the amine.

	Calc. for $C_6H_4\begin{cases}CONHC_6H_5\\COONH_3CH_2C_6H_5.\end{cases}$	Found.
$C_6H_5CH_2NH_2$	30·74	31·17

5. *Methylamine Phthalamate*, $C_6H_4\begin{cases}CONH_2\\COONH_3CH_3.\end{cases}$

The substance, prepared from methylamine and phthalamic acid,[1] consists of colourless needle-shaped crystals: it is soluble in alcohol and water, but not in ether: melts at 146°–148°: and decomposes into methylamine and phthalamide, when treated with water, acid, or alkali. The substance was analysed and gave the following result:

0·3 grm. the substance gave, 0·045 grm. the amine.

	Calc. for $C_6H_4\begin{cases}CONH_2\\COO\cdot NH_3CH_3.\end{cases}$	Found.
CH_3NH_2	15·89	15·00

6. *Aniline Phthalamate*, $C_6H_4\begin{cases}CONH_2\\COONH_3C_6H_5.\end{cases}$

[1] Ber. d. chem. Gesell., **19**, 1402; Amer. Chem. Journ. **3**, 29.

The substance, obtained from aniline and phthalamic acid, is soluble in alcohol, but not in ether: it melts at 185°–187°.

0·5 grm. of salt gave, 0·1803 grm. the amine.

	Calc. for $C_6H_4\begin{cases}CONH_2\\COONH_3C_6H_5.\end{cases}$	Found.
$C_6H_5NH_2$	36·82	36·07

7. *Methylamine Phenylsuccinamate*, $C_2H_4\begin{cases}CONHC_6H_5\\COONH_3CH_3.\end{cases}$

The salt, formed from methylamine and phenylsuccinamic acid, consists of colourless needles: it is soluble in water or alcohol, but not in ether or benzene: and melts at 115°–120°. Its analysis gave the following result:

0·5 grm. the substance gave, 0·07 grm. the amine.

	Calc. for $C_2H_4\begin{cases}CONHC_6H_5\\COONH_3CH_3.\end{cases}$	Found.
CH_3NH_2	13·84	14·00

In conclusion, I have to thank Prof. M. Kuhara for the advice he has given in carrying out this research.

June, 1908.

[1] Ann. d. Chem., **68**, 28.

INDEX OF AUTHORS.

PAGE

AOYAGI, E.,—A Graphical Representation of Potential Drops and Distribution of Currents in a Network System, ... 40

CHIKASHIGE, M.,—Action of Alcohol upon Mercury Perchlorates, ... 145

CHIKASHIGE, M.,—See M. KUHARA and M. CHIKASHIGE.

CHIKASHIGE, M., and H. MATSUMOTO,—Defects of Uncarburetted Water-Gas as Fuel for Laboratory Use, ... 55

HIKI, T.,—On the Allanite Crystal from Hiei Mountain, ... 72

HIKI, T.,—Occurrence of Cerasite and Chiastolite in a Metamorphosed Clay Slate 125

HORI, K.,—see S. TANABE and K. HORI.

IKAWA, K.,—Kinetics of the Hydrolytic Decomposition of Methyl Acetate by the Catalytic Action of Acetic Acid, ... 320

IKAWA, K.,—Kinetics of Two Simultaneous Reactions in a System... 375

KAINOSHO, T.,—see M. KUHARA and T. KAINOSHO.

KASHIWAGI, Y.,—Short Period Magnetographs, ... 217

KATO, Y.,—Physico-chemical Studies on *Tofu*, ... 325

KATO, Y.,—The Electrical Conductivity and Dissociation of Sulphuric Acid in Aqueous Solutions at Higher Temperatures, ... 332

KATO, Y.,—On the Reaction between Ferric Chloride and Potassium Ferricyanide, ... 352

KIMURA, M.,—On the Dirichlet's Principle, ... 414

KIMURA, M.,—Motion of a Negative Electric Charge in the Field due to an Electric Doublet, ... 420

KISHI, Y.,—see M. KUHARA and Y. KISHI.

KOMATSU, S.,—Amine Salts of Phthalamic, Phenylphthalamic, and Phenylsuccinamic Acids, ... 431

KOMATSU, S.,—see K. KUHARA and S. KOMATSU.

KUHARA, M., and M. CHIKASHIGE,—Synthesis of Indigo and its Derivatives, ... 1

KUHARA, M., and M. CHIKASHIGE,—Note on the Influence of Solvents upon the Formation of Chloracetyldiphenylamine, ... 87

KUHARA, M., and T. KAINOSHO,—On Beckmann's Rearrangement, ... 254

KUHARA, M., and Y. KISHI,—Action of Ammonia and Amines upon Chloral,.. 114

KUHARA, M., and S. KOMATSU,—Isomeric Phenylphthalimides and Some Allied Compounds, ... 391

KUHARA, M., and M. MATSUI,—Formation of Amines from the Halogen Imido Esters,... 187

MATSUI, M.,—Action of Hydrogen Sulphide upon Imido esters,... 285

PAGE
MATSUI, M.,—Oxidation of Hydrochinone by the Catalysis of Carbon, ... 386
MATSUI, M.,—see M. KUHARA and M. MATSUI.
MATSUMOTO, H.,—Note on the Body of Awata Pottery, ... 77
MATSUMOTO, H.,—see M. CHIKASHIGE and H. MATSUMOTO.
MIZUNO, T.,—On the Filings Coherer and Wireless Telegraphy, ... 28
MIZUNO, T.,—Electric Resonance, ... 33
MORI, Y.,—Electrolytic Dissociation of Partially Neutralised Weak Acids, ... 205
MURAOKA, H.,—Über eine einfache Methode, den Grundton eines Klanges, dessen Höhe um eine Octave unsicher ist, zu entscheiden, ... 211
MURAOKA, H., and T. TAMARU,—Über die Veränderung der elektrischen Leitungsfähigkeit eines Pulvers durch Induktion, ... 20
OGAWA, K.,—On the Electromagnetic Screening Effect of Metallic Conductors, 140
OKADA, S.,—Note on the Action of Phosphorus Pentachloride upon Tartranil, 168
OSAKA, Y.,—On the Distribution of Iodine between Two Solvents,... 93
OSAKA, Y.,—On the Equilibrium of the Electrolytic Dissociation of Partially Neutralised Acids and Bases,... 103
OSAKA, Y.,—Reaction between Silver Nitrate and Disodium Hydrogen Phosphate,... 158
OSAKA, Y.,—Determination of the Solubility of a given Substance by Means of Pulfrich's Refractometer, ... 265
OSAKA, Y., ——— II. 290
OSAKA, Y.,—On the Birotation of d-Glucose. II., ... 304
OSAKA, Y., and J. YAMASAKI,—Equilibrium between Reciprocal Salt Pairs, ... 173
OTAKE, T.,—On the Theory of the Rotary Converter, ... 228
SAITO, D.,—Notes on the Refining of Copper, ... 195
SHIOMI, T.,—On the Solubility of Disodium Hydrogen Phosphate in Water,... 406
TAMARU, T.,—see H. MURAOKA and T. TAMARU.
TANABE, S.,—Deflection and Vibration Diagrams of Kinokawa Railway Bridge Truss,... 75
TANABE, S.,—Retardation Tests with an Unloaded, Covered Railway Wagon,... 137
TANABE, S., and K. HORI,—Dynamometer Car Experiments. Part I. 277
WATANABE, T.,—Versuche zur Nutzbarmachung von Metallabfällen,... 183
YAMASAKI, J.,—Reaction between Carbonic Acid and Lead Acetate in an Aqueous Solution, ... 173
YAMASAKI, J., ——— II. 275
YAMASAKI, J.,—see Y. OSAKA and J. YAMASAKI.
YOKOBORI, J.,—On the Solubility of Gold-Silver Alloys in Potassium Cyanide Solutions, ... 65

INDEX OF SUBJECTS.

PAGE

Acetic acid, catalytic action of, on the hydrolytic decomposition of methyl acetate (*Ikawa*), ... 320
Acids and bases, partially neutralised, electrolytic dissociation of (*Osaka*), ... 103
Acids, partially neutralised, electrolytic dissociation of (*Mori*), ... 205
Action of alcohol upon mercury perchlorates (*Chikashige*), ... 145
Action of ammonia and amines upon chloral (*Kuhara* and *Kishi*), ... 114
Action of hydrogen sulphide upon imidoesters (*Matsui*), ... 285
Action of phosphorus pentachloride upon tartranil (*Okada*, ... 168
Alcohol, action of, upon mercury perchlorates (*Chikashige*), ... 145
Allanite crystal from Hiei Mountain (*Hiki*) ... 72
Alloys, gold-silver, its solubility in potassium cyanide solutions (*Yokoberi*, ... 65
Amine Salts of phthalamic, phenylphthalamic, and phenysuccinamic acids (*Komatsu*) 431
Ammônia, action of, and of amines upon chloral (*Kuhara* and *Kishi*), ... 114
Awata pottery, body of (*Matsumoto*), ... 77
Bases and acids, partially neutralised, electrolytic dissociation of (*Osaka*), ... 103
Beckmann's rearrangement (*Kuhara* and *Kainosho*), ... 254
Birotation of d-Glucose (*Osaka*), ... 304
Body of Awata pottery (*Matsumoto*), ... 77
Carbon, catalysis of, on the oxidation of hydroquinone (*Matsui*), ... 386
Carbonic acid and lead acetate, reaction between, in an aqueous solution (*Yamasaki*), ... 176, 275
Catalytic action of acetic acid on the hydrolytic decomposition of methyl acetate (*Ikawa*), ... 320
Cerasite and chiastolite, occurrence of, in a metamorphosed clay slate (*Hiki*), 125
Chloracetyldiphenylamine, influence of solvents upon the formation of (*Kuhara* and *Chikashige*), ... 87
Chloral, action of ammonia and of amines upon (*Kuhara* and *Kishi*), ... 114
Clay slate, metamorphosed, occurrence of cerasite and chiastolite in (*Hiki*) ... 125
Coherer, filings, and wireless telegraphy (*Mizuno*), ... 28
Conductors, metallic, the electromagnetic screening effect of (*Ogawa*), ... 140
Converter, rotatory, theory of (*Otake*), ... 228
Copper, refining of (*Saito*), ... 195
Currents, distribution of, in a network system (*Awoyagi*), ... 40
Defects of uncarburetted water gas as fuel for laboratory use (*Chikashige* and *Matsumoto*), ... 55
Deflection and vibration diagrams of Kinokawa railway bridge truss (*Tanabe*), 75
Determination of the solubility of a given substance by means of Pulfrich's refractometer (*Osaka*), ... 265, 290

PAGE
Dirichlet's principle (*Kimura*), ... 414
Disodium hydrogen phosphate and silver nitrate, reaction between (*Osaka*), ... 158
Disoduim hydrogen phosphate, its solulility in water (*Shiomi*),... 406
Dissociation and electric conductivity of sulphuric acid in aqueous solutions at higher temperatures (*Kato*), ... 332
Distribution of currents in a network system (*Awoyagi*), ... 40
Distribution of iodine between two solvents (*Osaka*), ... 93
Dynamometer car experiments (*Tanabe* and *Hori*), ... 277
Electric doublets, motion of a negative electric charge in the field due to (*Kimura*), ... 420
Electric resonance (*Mizuno*), ... 33
Electrical conductivity and dissociation of sulphuric acid in aqueous solutions at higher temperatures (*Kato*), ... 332
Electrolytic dissociation of partially neutralised weak acids (*Mori*),... 205
Electrolytic dissociation, equilibrium of, of partially neueralised acids and bases (*Osaka*), ... 103
Electromagnetic screening effect of metallic conductors (*Ogawa*), ... 140
Elektrische Leitfähigkeit eines Pulvers, deren Veränderung durch Induction (*Muraoka* and *Tamaru*),... 20
Equilibrium between reciprocal salt-pairs (*Osaka* and *Yamasaki*), ... 173
Equilibrium of electrolytic dissociation of partially neutralised acids and bases (*Osaka*), ... 103
Ferric chloride and postassium ferricyanide, reaction between (*Kato*), ... 352
Filings coherer and wireless telegraphy (*Mizuno*), ... 28
Formation of amines from the halogen imido esters (*Kuhara* and *Matsui*), ... 187
Fuel for laboratory use, defects of uncarburetted water gas as (*Chikashige* and *Matsumoto*), ... 55
d-Glucose, birotation of (*Osaka*), ... 304
Gold-silver alloys, solubility of, in potassium cyanide solutions (*Yokohori*), ... 65
Graphical representation of potential drops and distribution of currents in a network system (*Awoyagi*) 40
Grundton, dessen Entscheidung in Falle desselbe um eine Octave unsicher ist (*Muraoka*),... 211
Halogen imido esters, formation of amines from (*Kuhara* and *Matsui*, ... 187
Hiei mountain, allanite crystal from (*Hiki*), ... 72
Hydrogen sulphide, action of, upon imido esters (*Matsui*),... 285
Hydrolytic decomposition of methyl acetate by the catalytic action of acetic acid (*Ikawa*), ... 320
Hydroquinone, oxidation of, by the catalysis of carbon (*Matsui*), ... 386
Imidoesters, action of hydrogen sulphide upon (*Matsui*), ... 285
Induction, Veränderung der elektrischen Leitfähigkeit eines Pulvers durch (*Muraoka* and *Tamaru*),... 20
Indigo and its derivatives, synthesis of (*Kuhara* and *Chikashige*), ... 1

PAGE

Influence of solvents upon the formation of chloracetyldiphenylamine (*Kuhara* and *Chikashige*), ... 87
Iodine, distribution of, between two solvents (*Osaka*), ... 93
Isomeric phenylphthalimides and some allied compounds (*Kuhara* and *Komatsu*), ...
Kinetics of the hydrolytic decomposition of methyl acetate by the catalytic action of acetic acid (*Ikawa*), ... 320
Kinetics of two simultaneous reactions in a system (*Ikawa*), ... 375
Kinokawa railway bridge truss, deflection and vibration diagrams of (*Tanabe*), 75
Klang, methode den Grundton desselben zu entscheiden, wenn der letztere um eine Octave unsicher ist (*Muraoka*), ... 211
Lead acetate and carbonic acid, reaction between, in an aqueous solution (*Yamasaki*), ... 176, 275
Magnetographs, short period (*Kashiwagi*), ... 217
Mercury perchlorates, action of alcohol upon (*Chikashige*),... 145
Metallabfällen, Versuche zur Nutzbarmachung von (*Watanabe*),... 183
Metallic conductors, electromagnetic screening effect of (*Ogawa*), ... 140
Metamorphosed clay slate, occurrence of cerasite and chiastolite in (*Hiki*), ... 125
Methyl acetate, hydrolytic decomposition of, by the catalytic action of acetic acid (*Ikawa*), ... 320
Motion of a negative electric charge in the field due to an electric doublet (*Kimura*), ... 420
Negative electric charge, motion of, in the field due to an electric doublet (*Kimura*), ... 414
Network system, distribution of currents in (*Aoyagi*), ... 40
Nutzbarmachung von Metallabfällen (*Watanabe*), ... 183
Occurrence of cerasite and chiastolite in a metamorphosed clay slate (*Hiki*),... 125
Oxidation of hydroquinone by the catalysis of carbon (*Matsui*), ... 386
Phenylphthalimides, isomeric, and allied compounds (*Kuhara* and *Komatsu*),... 391
Phosphorus pentachloride, action of, upon tartranil (*Okada*), ... 168
Phthalamic, phenylphthalamic, and phenylsuccinamic acids, amine salts of (*Komatsu*), ... 431
Physico-chemical studies on tofu (*Kato*),... 325
Potassium cyanide solutions, solubility of gold-silver alloys in (*Yokobori*), ... 65
Potassium ferricyanide and ferric chloride, reaction between, (*Kato*). 352
Potential drops, graphical representation of (*Awoyagi*), ... 40
Principles, Dirichlet's (*Kimura*), ... 414
Pulfrich's refractometer, determination of the solubility of a given substance by means of (*Osaka*), ... 265, 290
Pulver, Veränderung der elektrischen Leitfähigkeit desselben durch Induction (*Muraoka*), ... 20
Railway wagon, unloaded, covered, retardation tests with, (*Tanabe*), ... 57

PAGE

Reaction between carbonic acid and lead acetate in an aqueous solution (*Yamasaki*), ... 176, 275
Reaction between ferric chloride and potassium ferrocyanide (*Kato*), ... 352
Reaction between silver nitrate and disodium hydrogen phosphate (*Osaka*), ... 158
Rearrangement, Beckmann's (*Kuhara* and *Kainosho*), ... 254
Reciprocal salt pairs, equilibrium between (*Osaka* and *Yamasaki*), ... 173
Refining of copper (*Saito*), ... 195
Refractometer, Pulfrich's, determination of the solubility of a given substance by means of (*Osaka*), ... 265, 290
Resonance, electric (*Mizuno*), ... 33
Retardation tests with an unloaded, covered railway wagon (*Tanabe*), ... 137
Rotary converter, theory of (*Otake*), ... 228
Screening effect, electromagnetic, of metallic conductors (*Ogawa*), ... 140
Short period magnetographs (*Kashiwagi*), ... 217
Silver-gold alloys, solulbility of, in potassium cyanide solutions (*Yokobori*), ... 65
Silver nitrate and disodium hydrogen phosphate, reaction between (*Osaka*), ... 158
Solubility, determination of, of a given substance by means of Pulfrich's refractometer (*Osaka*), ... 265, 290
Solubility of disodium hydrogen phosphate in water (*Shiomi*), ... 406
Solubility of gold-silver alloys in potassium cyanide solutions (*Yokobori*), ... 65
Solvents, influence of, upon the formation of chloracetyldiphenylamine (*Kuhara* and *Chikashige*), ... 87
Sulphuric acid, electric conductivity and dissociation of, in aqueous solutions at higher temperatures (*Kato*), ... 332
Synthesis of indigo and its derivatives (*Kuhara* and *Chikashige*), ... 1
Tartranil, action of phosphorus pentachloride upon (*Okada*), ... 168
Telegraphy, wireless and filings coherer (*Mizuno*) 28
Theory of the rotary converter (*Otake*), ... 228
Tofu, physico-chemical studies on (*Kato*), ... 325
Two simultaneous reactions, kinetics of (*Ikawa*), ... 375
Uncarburetted water gas, defects of, as fuel for laboratory use (*Chikashige* and *Matsumoto*), ... 55
Versuche zur Nutzbarmachung von Metallabfällen, (*Watanabe*), ... 183
Vibration and deflection diagrams of Kinokawa railway bridge truss (*Tanabe*), 75
Water gas, defects of uncarburetted, as fuel for laboratory use (*Chikashige* and *Matsumoto*), ... 55
Wireless telegraphy and filings coherer (*Mizuno*), ... 28

明治四十二年三月十八日印刷
明治四十二年三月廿一日發行

編纂兼發行者　京都帝國大學理工科大學

印刷者　東京市京橋區築地三丁目十一番地
野村宗十郎

印刷所　東京市京橋區築地二丁目十七番地
株式會社東京築地活版製造所

CONTENTS.

Action of Hydrogen Sulphide upon Imidoesters. PAGE
By Motooki Matsui 285

Determination of the Solubility of a Given Substance by Means of Pulfrich's Refractometer. II.
By Yukichi Osaka 290

On the Birotation of d-Glucose. II.
By Yukichi Osaka 304

Kinetics of the Hydrolytic Decomposition of Methyl Acetate by the Calalytic Action of Acetic Acid.
By Kozo Ikawa 320

Physico-chemical Studies on Tofu.
By Yogoro Kato 325

The Electrical Conductivity and Dissociation of Sulphuric Acid in Aqueous Solutions at Higher Temperatures.
By Yogoro Kato . . , ... 332

On the Reaction between Ferric Chloride and Potassium Ferricyanide.
By Yogoro Kato 352

Kinetics of Two Simultaneous Reactions in a System.
By Kozo Ikawa 375

Oxidation of Hydroquinone by the Catalysis of Carbon.
By Motooki Matsui 386

Isomeric Phenylphthalimides and some Allied Compounds.
By Mitsuru Kuhara and Shigeru Komatsu . . 391

On the Solubility of Disodium Hydrogen Phosphate in Water.
By Tsutomu Shiomi 406

On the Dirichlet's Principle.
By Masamichi Kimura 414

Motion of a Negative Electric Charge in the Field due to an Electric Doublet.
By Masamichi Kimura 420

Amine Salts of Phthalamic, Phenylphthalamic, and Phenylsuccinamic Acid.
By Shigeru Komatsu 431